**Chemical Reaction Engineering-I**
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**Lecture 08**

# Integral Method of Analysis of Batch Reactor Data- Part 1

Welcome to the second lecture of module 3. In this module we are discussing, analysing the batch Reactor kinetic data by integral method of analysis so before going to this lecture let us have brief recap on our previous lecture.

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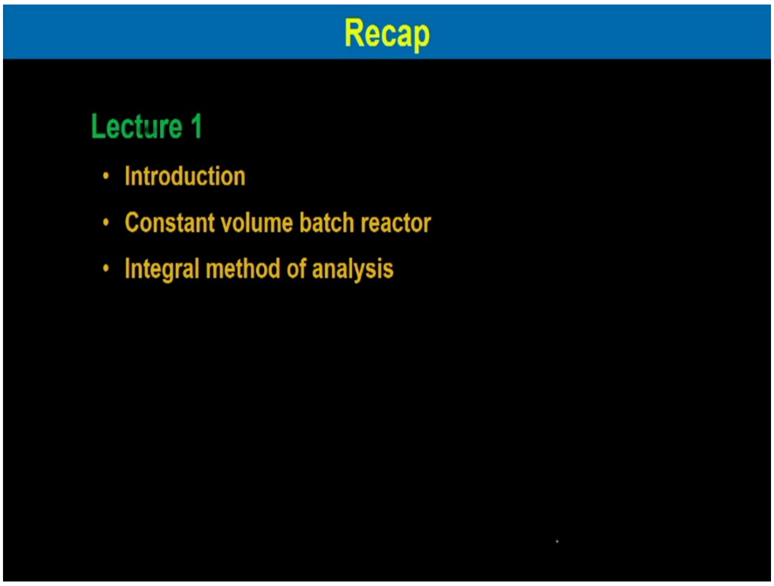

Recap

Lecture 1

- Introduction
- Constant volume batch reactor
- Integral method of analysis

So, in lecture 1 we consider Introduction to batch reactor data analysis and then we have considered the constant volume batch reactor kinetic data and then which method of analysis is better, whether integral method of analysis or batch reactor or differential method of analysis, we have discussed among their advantage and disadvantage. And we considered for certain irreversible reaction systems, we have analysed by integral method of analysis some of the data.

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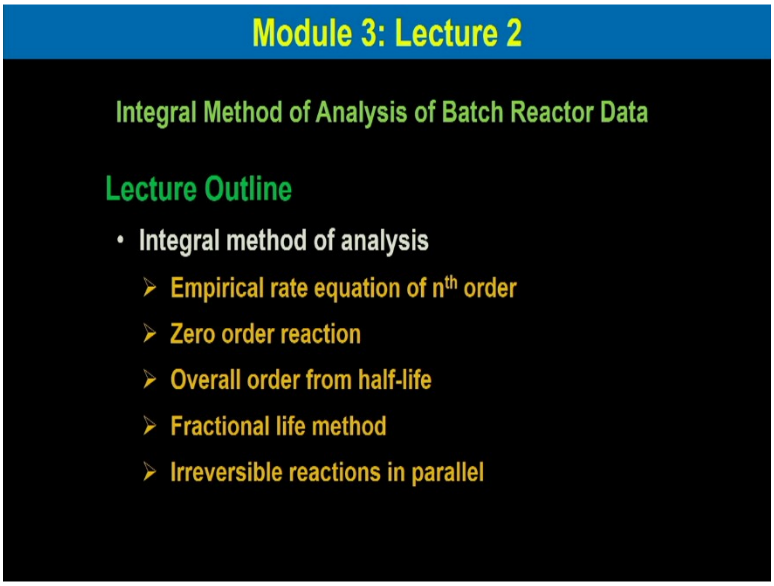

## Module 3: Lecture 2

Integral Method of Analysis of Batch Reactor Data

Lecture Outline

- Integral method of analysis
  - Empirical rate equation of nth order
  - Zero order reaction
  - Overall order from half-life
  - Fractional life method
  - Irreversible reactions in parallel

Now in this lecture we will continue our discussion on integral method of analysis of batch Reactor data and a brief outline of this lecture is integral method of analysis under which we will consider empirical rate equation of nth order, then we will consider zero order reactions, we will consider overall order of the reactions from half-life then fractional life method to obtain the kinetic equations, and we will also consider irreversible reactions in parallel so parallel irreversible reactions.

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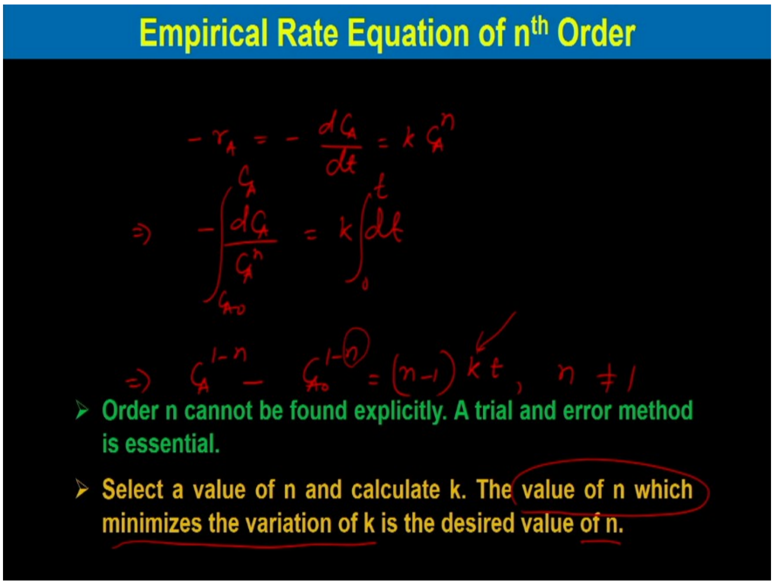

## Empirical Rate Equation of nth Order

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

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

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

- Order n cannot be found explicitly. A trial and error method is essential.
- Select a value of n and calculate k. The value of n which minimizes the variation of k is the desired value of n.

So, let us start with empirical rate equations of nth order, so when the order of the reactions of the reaction mechanism are not known for a particular reactions, we can consider a general order of the reactions and find out what is the actual order of the reaction to fit the particular nth order kinetics and we can then find out the order of the reactions.

Now let us form a general form of the rate equation of nth order which is

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

Now, if we integrate after separation of the variables like we can write

$$\Rightarrow -\frac{dC_A}{C_A^n} = kdt$$

and then if we integrate with the initial and boundary conditions which is

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

we will obtain

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

and this is valid when n is not equal to 1, so for $n \neq 1$ this integral form of the equation is valid.

So the calculation of the order of the reaction is not straightforward in this case as you can see this is a trial and error procedure so order n cannot be found explicitly, a trial and error method is essential. How we do the trial and error method? Select a value of n, so we need to select a particular value of n and then calculate k. So if we select n then from the analysis of concentration versus time history of the batch reactor data we can calculate K.

Now the values of n which minimises the variation of k is the desired value of n, so we need to check the value at which values of n which will minimise the variation of the rate constant or rate coefficient that will be the order of the reactions, we will later analyse this with an example.

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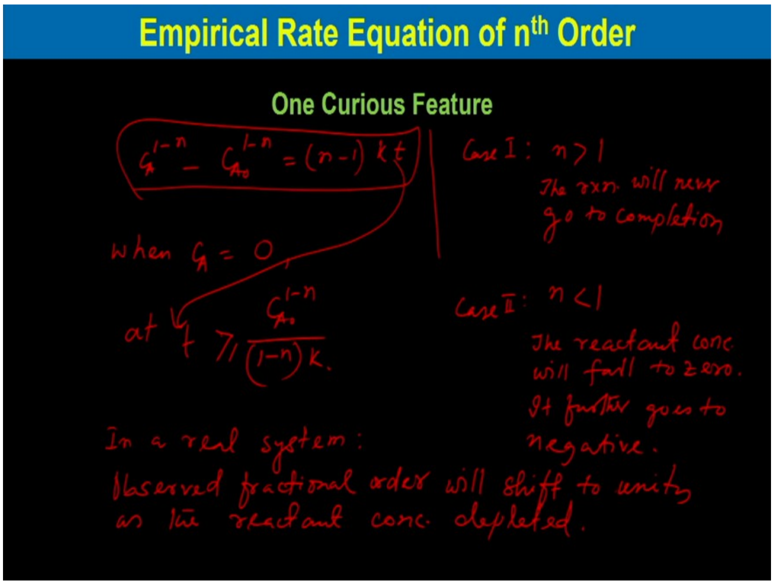

Empirical Rate Equation of n<sup>th</sup> Order

One Curious Feature

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

when $C_A = 0$

at $t \geq \frac{C_{A0}^{1-n}}{(1-n)k}$.

Case I: $n > 1$

The rxn will never go to completion

Case II: $n < 1$

The reactant conc will fall to zero. It further goes to negative.

In a real system:

Observed fractional order will shift to unity as the reactant conc. depleted.

Now, one curious feature of this rate form is that the rate equations let me write

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

Now, if you consider case 1, $n > 1$

If n greater than 1 from this expression you could see that the reactions will never go for completion so the reaction will never go to completion.

Case 2, if $n < 1$ what will happen? The reaction concentration will fall to zero and then move to negative as you increase the time, so it further goes to negative, the negative concentration is not possible so we should not carry out the integration till a certain time up to which the concentration of the reactants falls to zero, so that we can calculate when $C_A$ is equal to zero, the time would be

$$t \quad \frac{C_{A0}^{1-n}}{(1-n)k}$$

So if you substitute

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

over here in this rate expression,

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

if you substitute this t then you will find that $C_A$ would be zero, so we should not carry out the integration above this time, so $t \quad \frac{C_{A0}^{1-n}}{(1-n)k}$. So as a consequence of this in the real system what we observe, the fractional order reaction shifts to first order reaction or the order of the reaction becomes unity, so in a real system we can observe that fractional order will shift to unity as the reactant concentration depleted so this we need to consider while analysing nth order reaction.

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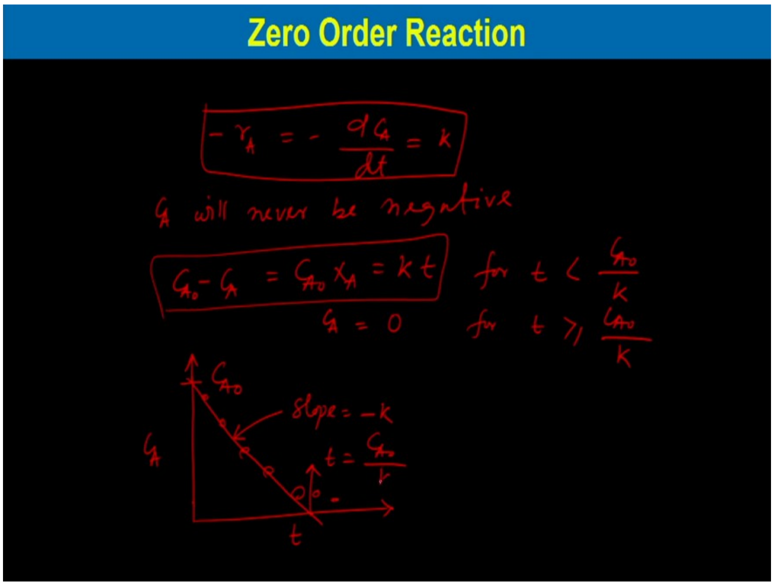

Zero Order Reaction

$$\boxed{-r_A = -\frac{dC_A}{dt} = k}$$

$C_A$ will never be negative

$$\boxed{C_{A0} - C_A = C_{A0}X_A = kt} \quad \text{for } t < \frac{C_{A0}}{k}$$

$$C_A = 0 \quad \text{for } t \geq \frac{C_{A0}}{k}$$

Now let us consider zero order reaction, as the order of the reaction suggest if it is zero order reaction then the rate of the reaction will be independent of the concentration of the reactants. So we can write

$$-r_A = -\frac{dC_A}{dt} = k$$

because the rate expression will be independent of the concentration of the reactants. Now if we integrate this rate expression and we note that the concentration $C_A$ will never be negative, in that case we would obtain

$$C_{A0} - C_A = C_{A0}X_A = kt \text{, for } t < \frac{C_{A0}}{t}$$

and

$$C_A = 0 \text{ ,for } t > \frac{C_{A0}}{t}$$

Now if we plot concentration versus time, so we can see that this is $C_A$ and this is t. So if we plot for this we would obtain so this intersection would be $C_{A0}$ that is the initial concentration and slope of this curve is -k and the time at this location $t = \frac{C_{A0}}{t}$.

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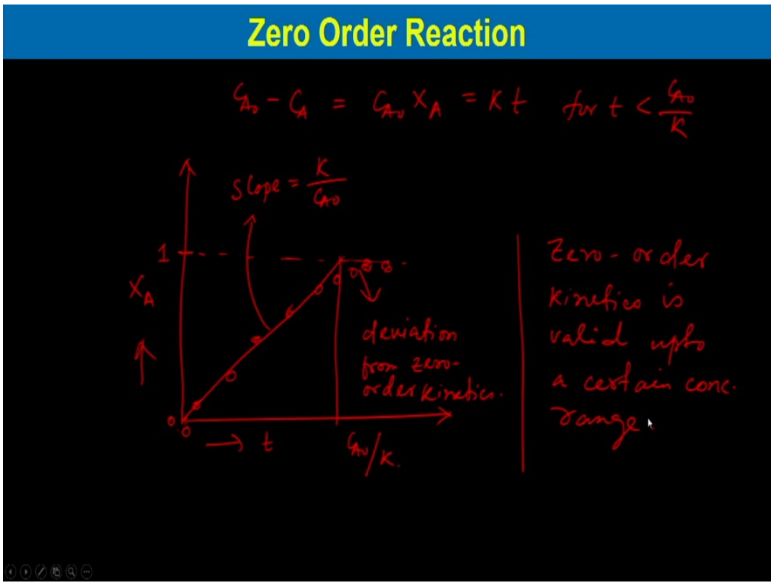

Zero Order Reaction

$C_{A0} - C_A = C_{A0} X_A = Kt$ for $t < \frac{C_{A0}}{K}$

Zero-order kinetics is valid upto a certain conc. range.

If you plot from here,

$$C_{A0} - C_A = C_{A0} X_A = kt$$

and that is valid for $t < \frac{C_{A0}}{t}$. Now, if we plot $X_A$ versus time, the curve will pass through the origin so it will pass through the origin and conversion from 0 to 1 say over here it is 1 and so the data so which you will find that up to time t is equal to $t = \frac{C_{A0}}{t}$, so this is the time you will get a linear equation in case of zero order reaction with conversion and time plot passing through the origin and the slope of this curve is $\frac{k}{C_{A0}}$.

And you can note that from the batch reactor data there is some deviation from the zero order kinetics, so this is the deviation at higher concentration deviation from zero order kinetics. So it means that maybe you will obtain the data like this, so that means as you close to the conversion 1 or at higher conversion or higher concentration so when the reactant concentration falls very low level or the conversion goes higher, you will find that there is a deviation from the zero order kinetics, this means that the zero order kinetics is valid up to a certain concentration.

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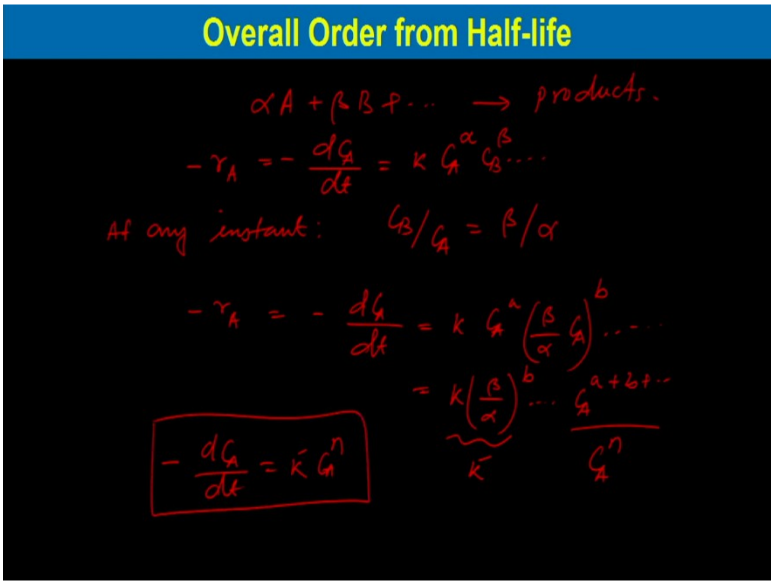

Overall Order from Half-life

$$\alpha A + \beta B + \cdots \rightarrow products.$$

$$-r_A = -\frac{dC_A}{dt} = k C_A^{\alpha} C_B^{\beta} \cdots$$

At any instant: $C_B/C_A = \beta/\alpha$

$$-r_A = -\frac{dC_A}{dt} = k C_A^{a}\left(\frac{\beta}{\alpha} C_A\right)^{b} \cdots$$

$$= \underbrace{k\left(\frac{\beta}{\alpha}\right)^{b} \cdots}_{k'} \underbrace{C_A^{a+b+\cdots}}_{C_A^{n}}$$

$$\boxed{-\frac{dC_A}{dt} = k' C_A^{n}}$$

Now, let us calculate the overall order of the reactions from the half-life method. So consider the irreversible reaction which is

$$\alpha A + \beta B + \ldots\ldots. \rightarrow products$$

And we can write the rate of the reactions for this is

$$-r_A = -\frac{dC_A}{dt} = k C_A^{\alpha} C_B^{\beta} \ldots\ldots\ldots$$

Now, if we write at any instant, we can write this

$$\frac{C_B}{C_A} = \frac{\beta}{\alpha}$$

this means that the stoichiometric ratio of the component A and B which was present initially will maintain the same stoichiometric ratio at any time.

So we can write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a\left(\frac{\beta}{\alpha}C_B\right)^b ........$$

So which you can write

$$= k\left(\frac{\beta}{\alpha}\right)^b .......C_A^{a+b+.....}$$

So this we can represent $k\left(\frac{\beta}{\alpha}\right)^b$ as $k^{'}$ and this we can represent $C_A^{a+b+.....}$ as $C_A^n$, so this is the general reaction we can write in terms of the nth order reaction so

$$-\frac{dC_A}{dt} = k^{'}\cdot$$

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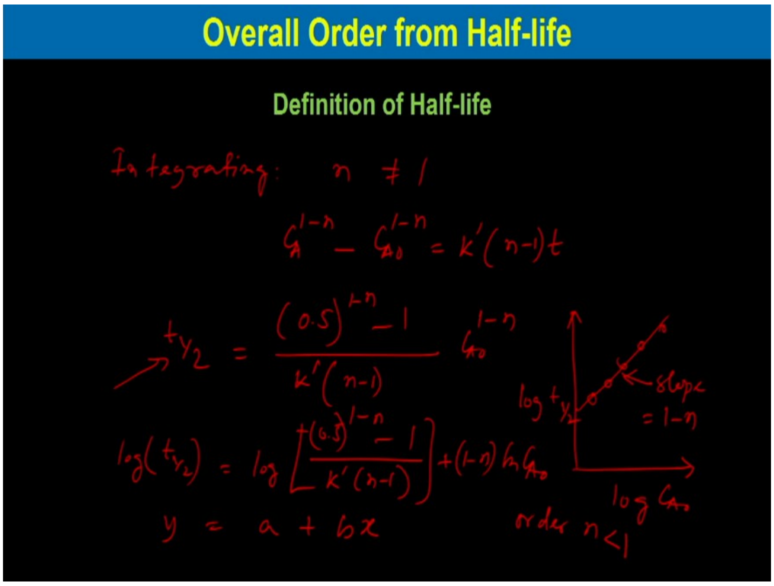

Overall Order from Half-life

Definition of Half-life

Integrating: $n \neq 1$

$$C_A^{1-n} - C_{A0}^{1-n} = k'(n-1)t$$

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

$$\log(t_{1/2}) = \log\left[\frac{(0.5)^{1-n} - 1}{k'(n-1)}\right] + (1-n)\ln C_{A0}$$

$$y = a + bx$$

Now, if we integrate this relation we will obtain, integrating for $n \neq 1$ we would obtain

$$C_A^{1-n} - C_{A0}^{1-n} = k'(n-1)t$$

So now, if we define the half-life is the time taken for a reactant to reduce its concentration to half of its value that means from here you can write

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

So the concentration of the reactants which was initially present is reduced to its half of its value and the time taken to reach that value is the half-life, so half-life is defined with $t_{1/2}$.

Now, if we plot log $t_{1/2}$ versus log $C_{A0}$, so if we take log of this we will obtain

$$\log t_{1/2} = \log\left[\frac{(0.5)^{1-n} - 1}{k'(n-1)}\right] + (1-n)\log C_{A0}$$

so this is of the form $y = a + bx$. So if we plot this, we would obtain intersect, so this is of slope of this curve would be equal to $(1-n)$, and this is valid for order n less than 1.

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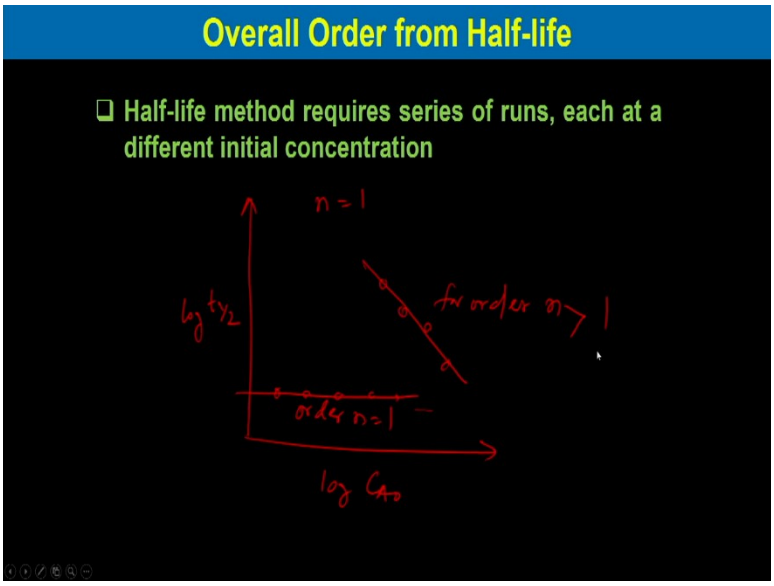

Overall Order from Half-life

- ❑ Half-life method requires series of runs, each at a different initial concentration

Now, half-life method requires a series of runs each at a different initial concentration. Now, if we plot with the same plot with a different initial concentration, we would see that when $n = 1$ we would obtain the curve of $\log t_{1/2}$ versus $\log C_{A0}$ would be independent of the initial concentration, so this is for order $n = 1$. Now for order n greater than 1, we will obtain a curve like this that means this is for order n greater than 1.

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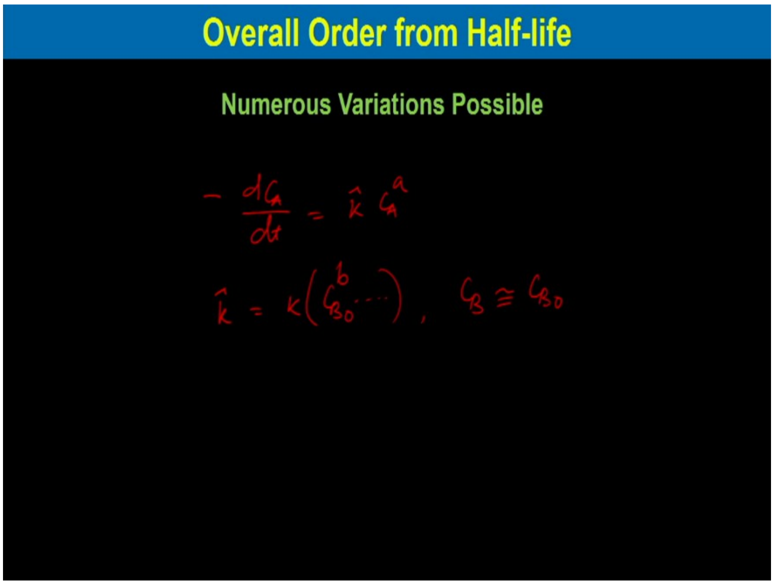

Overall Order from Half-life

Numerous Variations Possible

$$-\frac{dC_A}{dt} = \hat{k}\, C_A^{a}$$

$$\hat{k} = k\left(C_{B0}^{b} \cdots\right), \quad C_B \cong C_{B0}$$

So numerous variations of this half-life method is possible, let us for instance say for you have large number of components and say we have one component in large excess, say component A in large excess. So in that case we can write the general expression

$$-\frac{dC_A}{dt} = k^{'}C_{A0}^{a}$$

and this $k^{'}$ would be

$$k^{'} = k(C_{B0}^{b}......)$$

and so on and then $C_B$ would be approximately equal to $C_{B0}$, so this way we can have numerous variations of the fraction in a half-life method and we can obtain the integral forms of the rate equation which we would be able to solve for the kinetic data obtained from the batch reactor.

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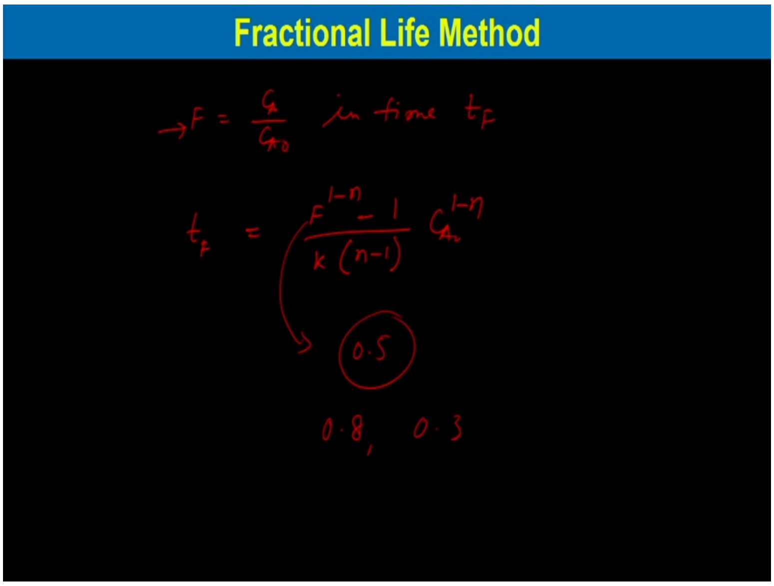

Fractional Life Method

$\rightarrow F = \frac{C_A}{C_{A0}}$ in time $t_F$

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

$\boxed{0.5}$

$0.8, \; 0.3$

Now, let us consider another variation which is called the Fractional Life method. So Fractional life method from the half-life we can write say for any fraction say consider a fraction F

$$F = \frac{C_A}{C_{A0}}$$

So the concentration of component A drops to any fraction f in $t_F$. So from the half-life equations we can write

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

Now this F we can put any values, it is not 0.5 that is half-life, it can be any value say the 0.8, 0.3 and so on, so this is an extension of the half-life method for any fractional conversion or any fractional change of the concentration at a particular time. Let us consider an example to find out kinetics using the factional order method.

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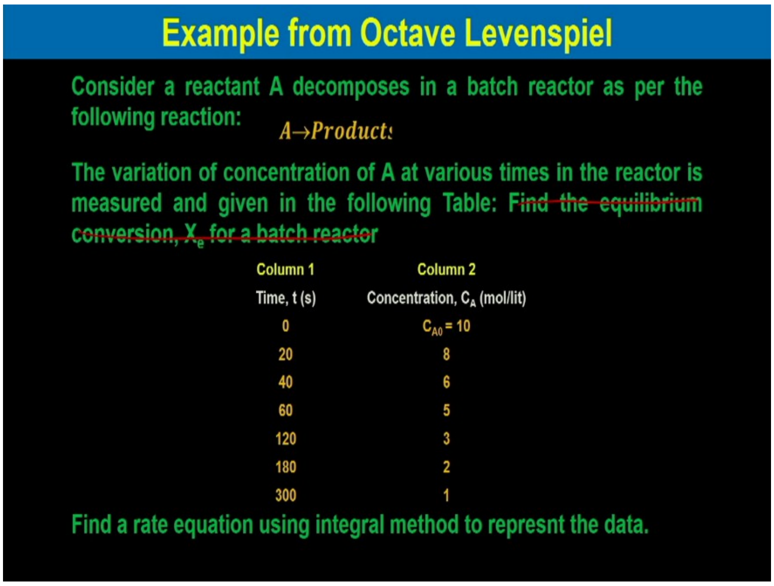

## Example from Octave Levenspiel

Consider a reactant A decomposes in a batch reactor as per the following reaction: $A \rightarrow Product$

The variation of concentration of A at various times in the reactor is measured and given in the following Table: ~~Find the equilibrium conversion, $X_e$ for a batch reactor~~

| Column 1<br>Time, t (s) | Column 2<br>Concentration, $C_A$ (mol/lit) |
|---|---|
| 0 | $C_{A0} = 10$ |
| 20 | 8 |
| 40 | 6 |
| 60 | 5 |
| 120 | 3 |
| 180 | 2 |
| 300 | 1 |

Find a rate equation using integral method to represnt the data.

Suppose consider a reactant A which decomposes in a batch reactor as per the following reactions. So, we have reactants A to products and the variation of concentration of A at various times in the reactor is measured and given in the following table. So this is the table which we can see that in column 1 we have time, at different time the concentration of the component A. We need to find out a rate equation using the integral method to represent the data.

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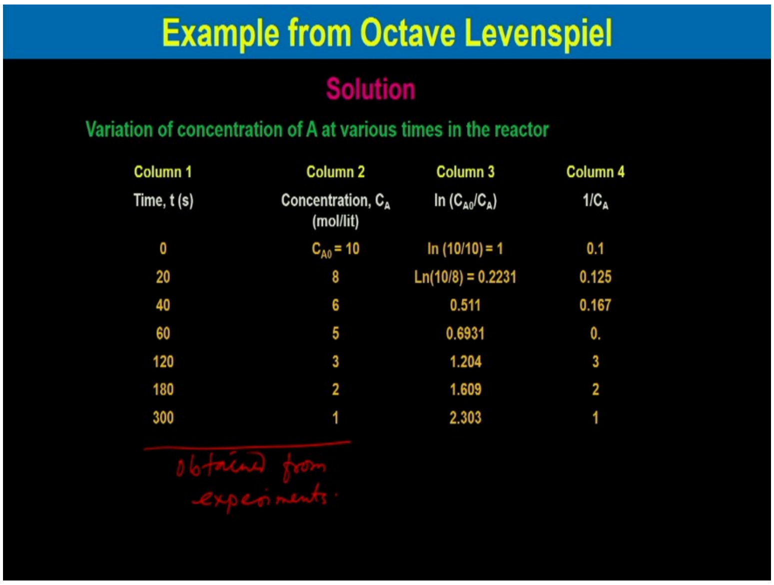

## Example from Octave Levenspiel

### Solution

Variation of concentration of A at various times in the reactor

| Column 1<br>Time, t (s) | Column 2<br>Concentration, $C_A$ (mol/lit) | Column 3<br>In $(C_{A0}/C_A)$ | Column 4<br>$1/C_A$ |
|---|---|---|---|
| 0 | $C_{A0} = 10$ | In (10/10) = 1 | 0.1 |
| 20 | 8 | Ln(10/8) = 0.2231 | 0.125 |
| 40 | 6 | 0.511 | 0.167 |
| 60 | 5 | 0.6931 | 0. |
| 120 | 3 | 1.204 | 3 |
| 180 | 2 | 1.609 | 2 |
| 300 | 1 | 2.303 | 1 |

obtained from experiments.

So variation of the concentration of A at various times in the batch reactor which is given, this is an example which is taken directly from the Levenspiel. So once we have the data, the time versus concentration from the batch reactor so this is basically the data which is obtained from the experiment. Now, if we calculate $\log\frac{C_{A0}}{C_A}$ and $\frac{1}{C_A}$ we can do that from this data so $\log C_{A0}$ is given which is 10 at initial time t=0, $C_{A0}$=10. So the initial concentration is given as 10 mole per litre, so we can calculate $\ln\frac{10}{10}$ is 1 here $\ln\frac{C_{A0}}{C_A}$. Similarly, $\ln\frac{10}{8}$ would be equal to 0.2231 and so on for all the other time and concentration we can calculate the log of initial concentration by concentration at any time.

Now, we can also calculate $\frac{1}{C_A}$ so which is basically the concentration which is initially which was present is 10 so $\frac{1}{10}$ is 0.1 and so on for all other concentrations at various times we can calculate $\frac{1}{C_A}$.

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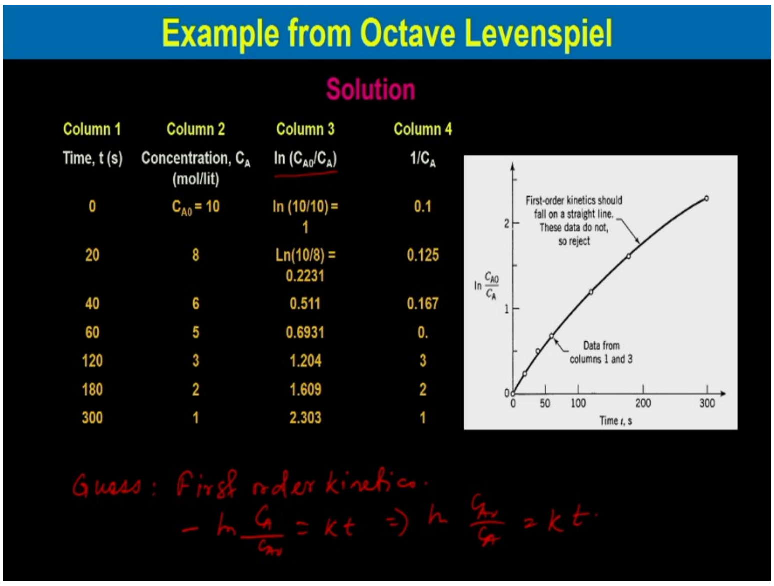

## Example from Octave Levenspiel

### Solution

| Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|
| Time, t (s) | Concentration, $C_A$ (mol/lit) | ln ($C_{A0}/C_A$) | $1/C_A$ |
| 0 | $C_{A0}$ = 10 | ln (10/10) = 1 | 0.1 |
| 20 | 8 | Ln(10/8) = 0.2231 | 0.125 |
| 40 | 6 | 0.511 | 0.167 |
| 60 | 5 | 0.6931 | 0. |
| 120 | 3 | 1.204 | 3 |
| 180 | 2 | 1.609 | 2 |
| 300 | 1 | 2.303 | 1 |

First-order kinetics should fall on a straight line. These data do not, so reject

Data from columns 1 and 3

Guess: First order kinetics.

$-\ln\frac{C_A}{C_{A0}} = kt \Rightarrow \ln\frac{C_{A0}}{C_A} = kt$.

Now the data which is given now, if we plot the time versus $\ln\frac{C_{A0}}{C_A}$, this we have plotted, let us guess the first-order kinetics. So if it is first-order kinetics, we know the for first order system

$$-\ln\frac{C_{A0}}{C_A} = kt$$

so we can write

$$\Rightarrow \ln\frac{C_{A0}}{C_A} = Kt$$

So if we plot $\ln\frac{C_{A0}}{C_A}$ versus time, it should give a straight line with a slope of K so we have plotted here the column 1 and column 3 so time versus the logarithmic $\frac{C_{A0}}{C_A}$, so as we can see the data is not fitted with a straight line so there is a deviation from the straight line so from this we can conclude that this does not follow the first order kinetics.

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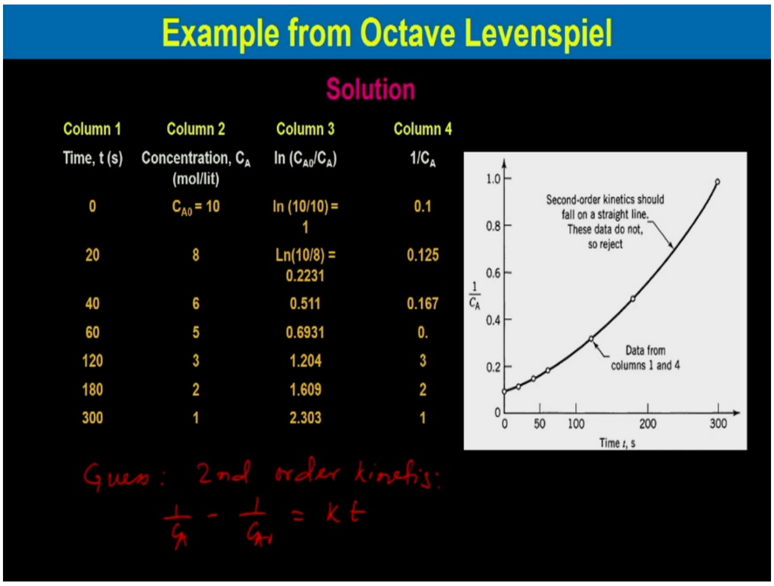

## Example from Octave Levenspiel

### Solution

| Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|
| Time, t (s) | Concentration, $C_A$ (mol/lit) | ln $(C_{A0}/C_A)$ | $1/C_A$ |
| 0 | $C_{A0} = 10$ | ln (10/10) = 1 | 0.1 |
| 20 | 8 | Ln(10/8) = 0.2231 | 0.125 |
| 40 | 6 | 0.511 | 0.167 |
| 60 | 5 | 0.6931 | 0. |
| 120 | 3 | 1.204 | 3 |
| 180 | 2 | 1.609 | 2 |
| 300 | 1 | 2.303 | 1 |

Guess: 2nd order kinetics:

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

Now, if we consider second order kinetics, so if we consider second order kinetics we can write

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

for the second order kinetics. So if we plot $\frac{1}{C_A}$ versus time, there will be intersect which is $\frac{1}{C_{A0}}$ and from slope we can calculate k, but this also does not fit with a straight line, so as we can see it does not follow the second order kinetics as well.

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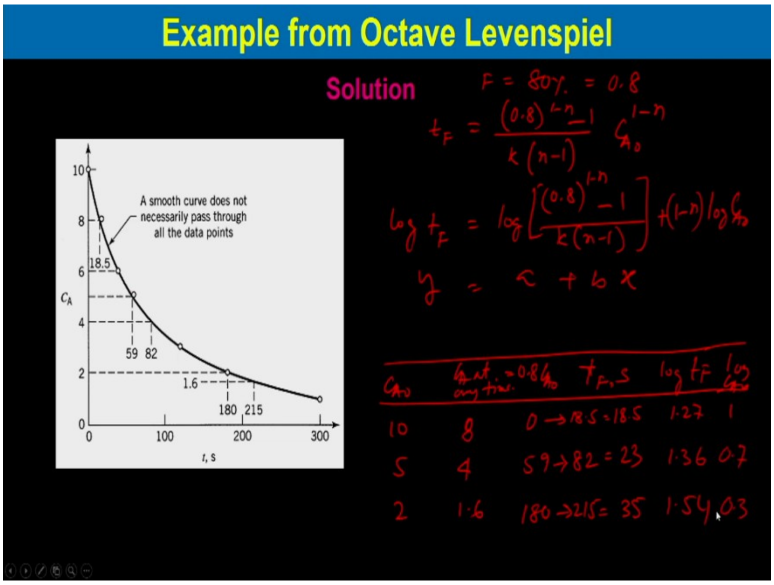

## Example from Octave Levenspiel

**Solution**

$F = 80\% = 0.8$

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}$$

$$\log t_F = \log\left[\frac{(0.8)^{1-n} - 1}{k(n-1)}\right] + (1-n)\log C_{A0}$$

$$y = a + bx$$

| $C_{A0}$ | $C_A$ at any time $= 0.8 C_{A0}$ | $t_F$, s | $\log t_F$ | $\log C_{A0}$ |
|---|---|---|---|---|
| 10 | 8 | $0 \rightarrow 18.5 = 18.5$ | 1.27 | 1 |
| 5 | 4 | $59 \rightarrow 82 = 23$ | 1.36 | 0.7 |
| 2 | 1.6 | $180 \rightarrow 215 = 35$ | 1.54 | 0.3 |

So now, consider a general nth order kinetics and find out the order of the reaction. So to do that let us plot concentration versus time feature given and then we can calculate say consider fractional life method $t_F$ is equal to say F fractional it reached the concentration to a fraction of $80\%$ so that means 0.8, so F = 0.8 so which is we can write

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}$$

Now, if we take the logarithmic as we have done before it will be

$$\log t_F = \log\left[\frac{(0.5)^{1-n} - 1}{k^{'}(n-1)}\right] + (1-n)\log C_{A0}$$

so this is of the form $y = a + bx$.

Now, if we plot concentration versus time, we obtain the table $C_{A0}$ which is say 10, 5 and 2, and $C_A$ at any time which reaches $0.8\,C_{A0}$, so that means we can calculate this would be 8, this would be 4 and this would be 1.6. So the time needed $t_F$ from this graph we can calculate $t_F$ would be from 0 to 18.5 so it will be 18.5 second, similarly if we see from here it is 59 seconds at this location so from 59 to 82 so the time change is 59 to 82 which is equal to 23.

And in this case we can see from 180 to 215, so we will take at any two different points and we can see the change in concentration with the time periods. So in this case we can see at this time we have 180 to 215 so which is equal to 35 seconds. So if we calculate $\log t_F$ of 18.5 which is equal to 1.27 similarly for others it would be 1.36 and 1.54 and similarly we can calculate $\log C_{A0}$ which is equal to 1.7 and 0.3.

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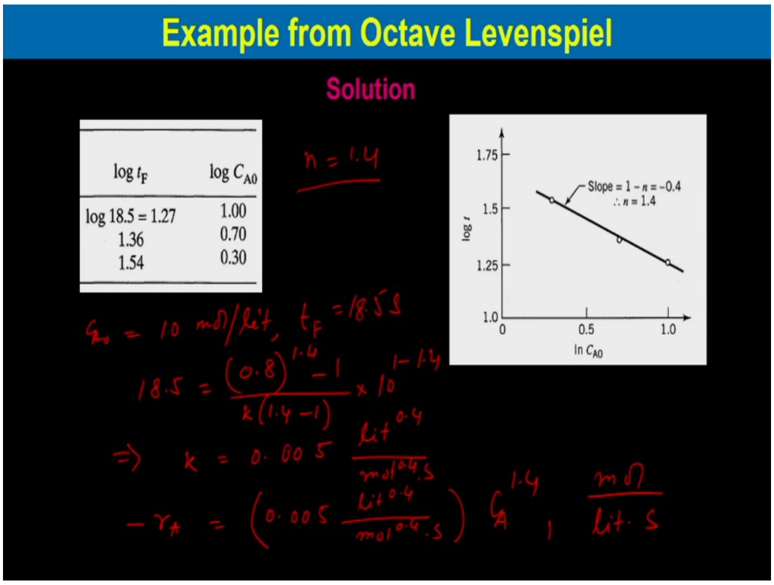

## Example from Octave Levenspiel

### Solution

| $\log t_F$ | $\log C_{A0}$ |
|---|---|
| $\log 18.5 = 1.27$ | 1.00 |
| 1.36 | 0.70 |
| 1.54 | 0.30 |

$n = 1.4$

$C_{A0} = 10$ mol/lit, $t_F = 18.5$ s

$$18.5 = \frac{(0.8)^{1.4} - 1}{k(1.4-1)} \times 10^{1-1.4}$$

$$\Rightarrow k = 0.005 \frac{lit^{0.4}}{mol^{0.4} s}$$

$$-r_A = \left(0.005 \frac{lit^{0.4}}{mol^{0.4} \cdot s}\right) C_A^{1.4}, \quad \frac{mol}{lit \cdot s}$$

So now, this is the $\log t_F$ and $\log C_{A0}$ we have calculated, now if we plot $\log t$ versus $\ln C_{A0}$, this will fit with a slope of $(n-1)$ which is about -0.4, so from the slope of this curve we can calculate that the n = 1.4, so this is order greater than 1 but it is fractional order. Now to evaluate the rate constant we pick up any concentration say $C_{A0}$ = 10 mole per litre and $t_F$ is 18.5 seconds, so if we put in the fractional order method we would get

$$18.5 = \frac{(0.8)^{1.4} - 1}{k(1.4-1)} * 10^{1-1.4}$$

From which we can calculate k

$$\Rightarrow k = 0.005 \frac{lit^{0.4}}{mol^{0.4} s}$$

So now we can write the complete rate expression which is

$$-r_A = (0.005 \frac{lit^{0.4}}{mol^{0.4} s}) C_A^{1.4}$$

and this has unit of rate is mole per litre second, so this way we can solve a particular kinetic data which is obtained from batch reactor and we can consider different kinetics and we can solve for the integral form of the rate equations and finally we can obtain the rate constant values and order of the reactions and we can propose the rate equations for that.

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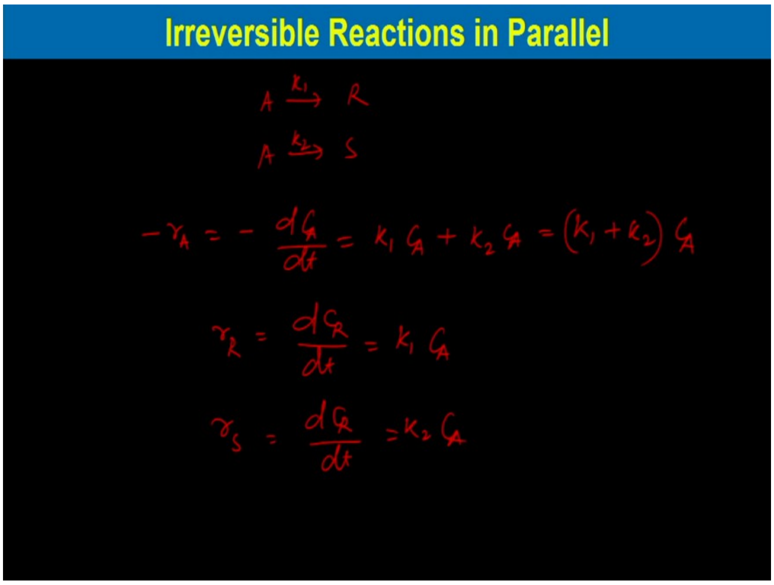

## Irreversible Reactions in Parallel

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

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

$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_R}{dt} = k_2 C_A$$

Now, let us consider an irreversible reaction which is in parallel reactions, suppose a reactant which is decomposing into two products that means

$$A \xrightarrow{K_1} R$$

$$A \xrightarrow{K_2} S$$

Both A and A is producing reactants R and S both are parallel reactions and we will consider these reactions are elementary reactions. So in that case the rate of the reactions we can write is

$$-r_A = -\frac{dC_A}{C_A} = K_1 C_A + K_2 C_A = (K_1 + K_2) C_A$$

Similarly we can write for the formation of R and S, so

$$r_R = \frac{dC_R}{dt} = K_1 C_A$$

and

$$r_S = \frac{dC_S}{dt} = K_2 C_A$$

so these are the 3 rate expressions; one is for the reactants and then other two is for the products. Now this is for the first time we are encountering with multiple reactions and if there are n number of reaction components then a single stoichiometric equation cannot give the concentration profile so we need to have n number of stoichiometric equations which would describe the concentration profile.

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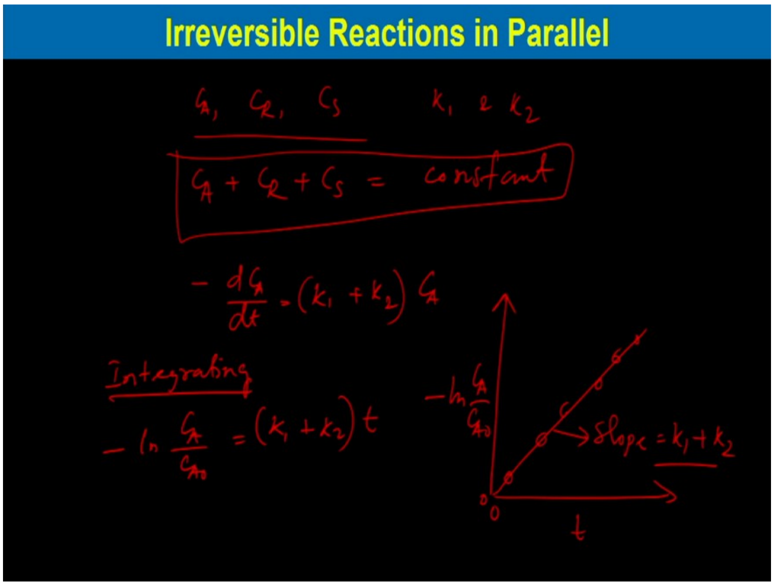

Irreversible Reactions in Parallel

$C_A, C_R, C_S$ $k_1$ & $k_2$

$\boxed{C_A + C_R + C_S = \text{constant}}$

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

Integrating

$-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2) t$

So for this system $C_A$, $C_R, C_S$ all of these alone cannot give the values of $K_1$ and $K_2$, so at least the concentration profile or we need to follow the concentration changes of the two species to get the $K_1$ and $K_2$. And this can be done following two species concentration change with a condition that the total concentration $C_A + C_R + C_S$ will remain constant at any time so then from this we can calculate the, any two concentration profile if we know then we can calculate the third concentration from the stoichiometric equation this equation.

So if we consider the first reaction which is

$$-\frac{dC_A}{dt} = (K_1 + K_2) C_A$$

So if we integrate this relation we would obtain

$$-\ln\frac{C_A}{C_{A0}} = (K_1 + K_2)t$$

So now, if we plot this $-\ln\frac{C_A}{C_{A0}}$ versus t if we plot so it will pass through the origin and from the slope we can obtain $K_1 + K_2$, so this integral form of this equation will give combination of $K_1$ and $K_2$.

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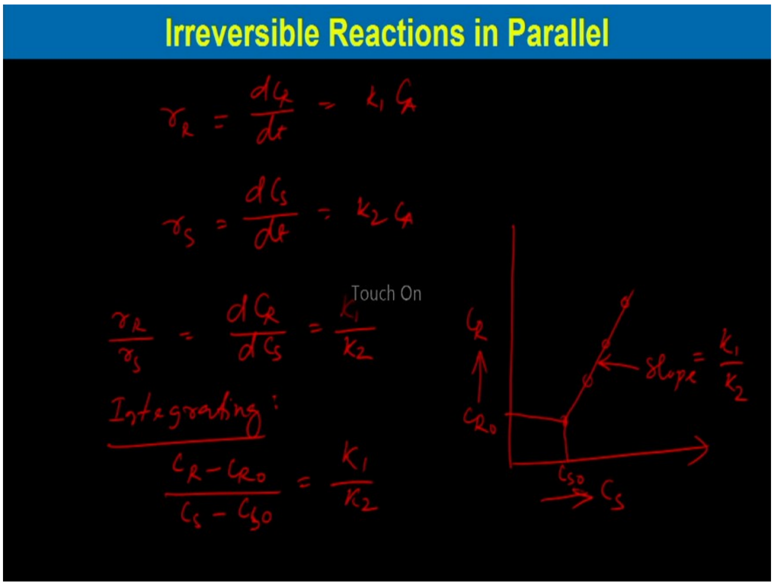

Irreversible Reactions in Parallel

$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

Integrating:

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{K_1}{K_2}$$

Now, if we divide the other two equations that is

$$r_R = \frac{dC_R}{dt} = K_1 C_A$$

and

$$r_S = \frac{dC_S}{dt} = K_2 C_A$$

if we divide these two we will obtain which is

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{K_1}{K_2}$$

So then we can integrate this equation and we simply obtain

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{K_1}{K_2}$$

So now, if we plot $C_R$ versus $C_S$ then we would be able to get a plot like this, so this is the initial concentration $C_{R0}$, this is $C_{S0}$ and from the slope of this curve we will obtain k1 by k2. So if we know from this $\frac{K_1}{K_2}$, and earlier we have obtained $\frac{K_1}{K_2}$ so then from these two relations we can calculate $K_1$ and $K_2$ individually.

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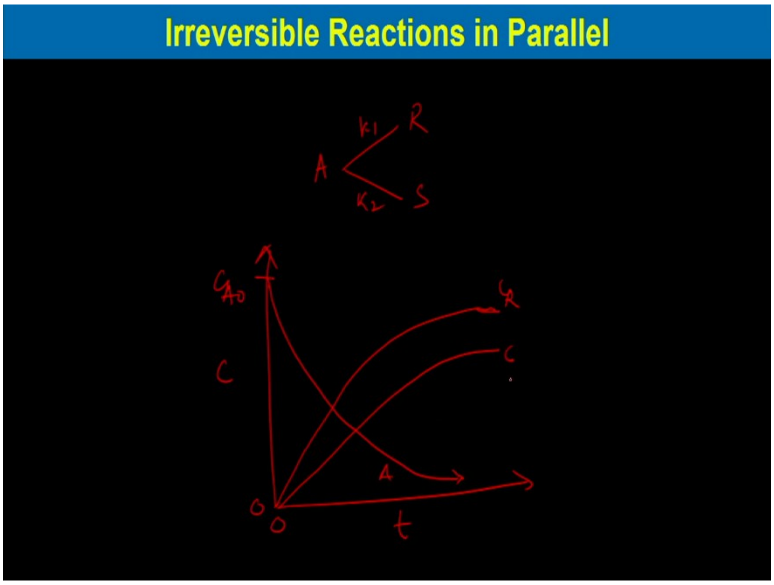

Irreversible Reactions in Parallel

Now for a typical case of this parallel reactions where

$$A \xrightarrow{K_1} R$$
$$A \xrightarrow{K_2} S$$

the concentration profile will look like concentration versus time. Concentration of A will gradually decrease with t so that means it starts with $C_{A0}$ and the profile it is for component A. Now for component R and S both will increase, so it depends on the rate of the individual $K_1$ and $K_2$, so this will be $C_R$ if $K_1$ is higher and this will be $C_S$, so this is the typical concentration profile for parallel reactions, so thank you very much for attending this lecture and we will continue our discussion on batch reactor data analysis for other reaction systems.