Chemical Reaction Engineering-I
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Lecture 07
Analysis of Batch Reactor Kinetic Data

Welcome to the first lecture of module 3. In this module we are going to discuss Interpretation or Analyses of the Batch Reactor Kinetic Data. Before going to this lecture let us have small recap of our earlier lectures which we had in module 2.

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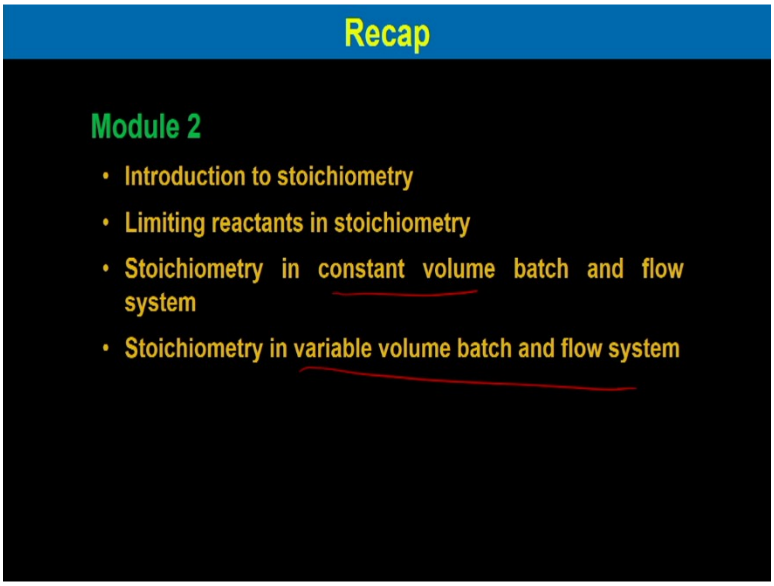

Recap

Module 2

- Introduction to stoichiometry
- Limiting reactants in stoichiometry
- Stoichiometry in constant volume batch and flow system
- Stoichiometry in variable volume batch and flow system

In module 2 we have basically covered stoichiometry and introduction to stoichiometry, then we have considered the limiting reactants in case of stoichiometry. We have considered two reactors; one is batch reactor and another is flow reactor and for both cases we have considered constant volume batch and flow reactor and how to obtain the stoichiometry in that system. And finally we have considered stoichiometry in variable volume batch and flow systems so each system we have completed with different examples.

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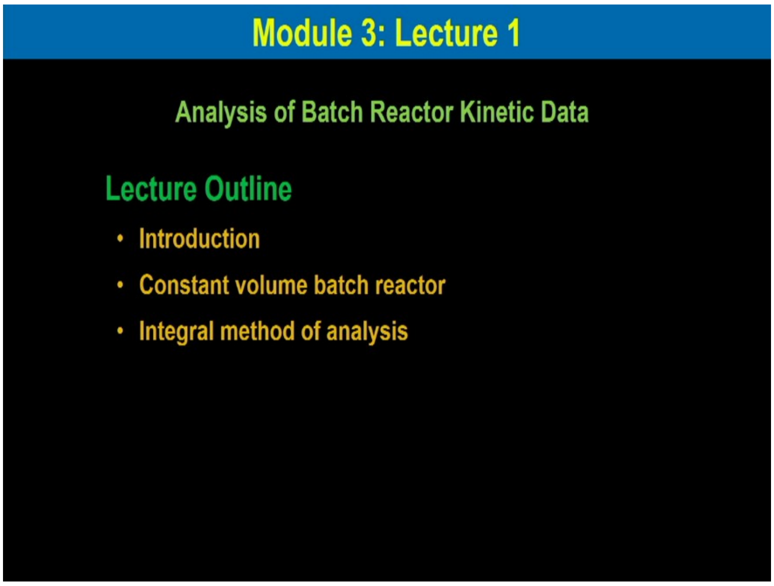

Module 3: Lecture 1

Analysis of Batch Reactor Kinetic Data

Lecture Outline

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

Now, in this lecture we will consider analyses of the batch Reactor Kinetic data. And the lecture outline would be introduction to the batch Reactor Kinetic data, then Constant volume batch reactor then we will consider integral method of analysis, so we will consider integral method of analysis in this lecture and to take the batch Reactor data and then we will analyse for different Kinetics.

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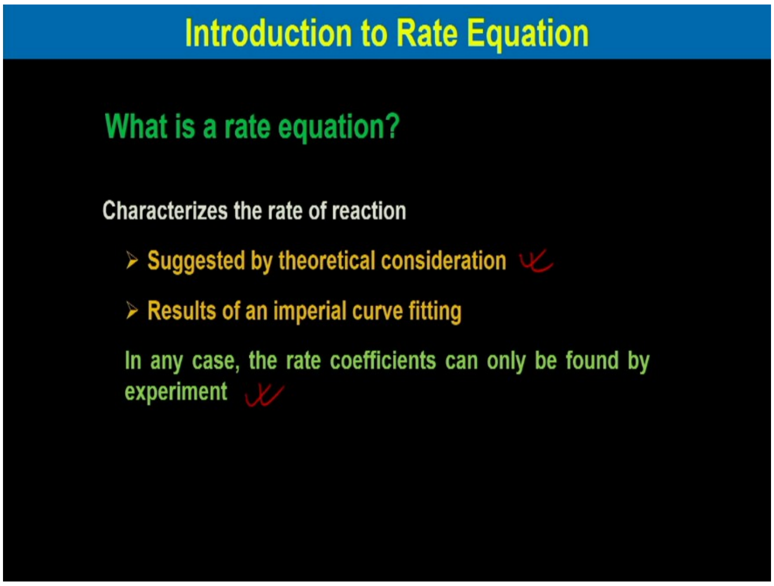

Introduction to Rate Equation

What is a rate equation?

Characterizes the rate of reaction

- Suggested by theoretical consideration ✓
- Results of an imperial curve fitting

In any case, the rate coefficients can only be found by experiment ✓

First we need to know that what is the rate equation? Although we have introduced at the beginning. Rate equation means it is the dependency of the concentration with the rate of the reaction, the reaction which happens if we represent them mathematically then we call rate of reactions. So, how to characterise the rate of reactions? We can characterise rate of reaction by suggested which can be obtained or suggested from theoretical consideration so theoretically we can obtain the rate expression or it can be obtained results of an imperial curve fitting. So in either case the rate coefficient can only be found by experiments, so whether it is imperial curve fitting or it is theoretical consideration whatever may be the rate of the reactions or the rate equation suggests, the constant value or the rate coefficient values can be obtained only by experiments. So we have to perform the experiments in different reactors and obtained the Kinetic data.

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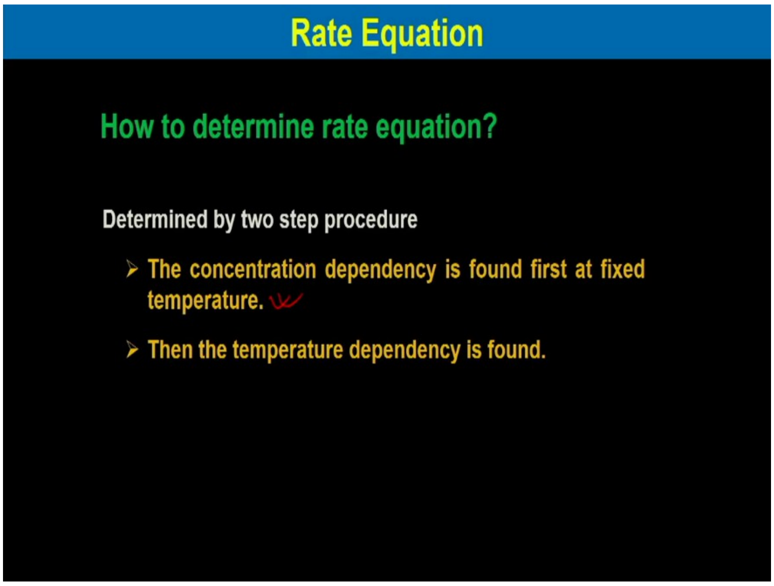

Rate Equation

How to determine rate equation?

Determined by two step procedure

- The concentration dependency is found first at fixed temperature.
- Then the temperature dependency is found.

How to determine rate equation? So we need to obtain the rate equations, but how we can obtain the rate equation? To obtain the rate equations we need to follow two different procedures; one of them is the concentration dependency is found first at fixed temperature and then the temperature dependency is found. So concentration dependency if we have to find out, we have to keep the condition isothermal, so we need to keep the temperature constant and vary the concentration and obtain the kinetics so then dependency of concentration can be obtained at a fixed temperature so that is the first thing we can do.

Now we have to fix the concentration and then we obtain the temperature dependency, we vary the temperature. So combine these two things will give the overall rate equation which is a function of temperature and concentration.

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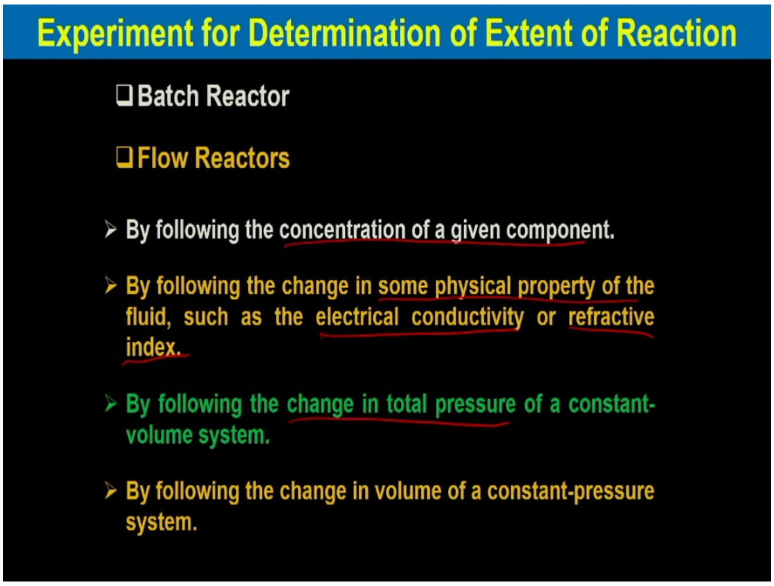

Experiment for Determination of Extent of Reaction

❑ Batch Reactor

❑ Flow Reactors

- By following the concentration of a given component.
- By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.
- By following the change in total pressure of a constant-volume system.
- By following the change in volume of a constant-pressure system.

Now experiment for determination of extent of reaction. So, how to obtain the extent of chemical reaction, how to determine experimentally? This can be obtained by two methods; one is using batch reactor or second is using flow reactor. So in case of batch or flow reactor the method we generally follow to obtain the extent of reactions we need to follow certain procedures.

We can do by following the concentration of given a components, so we can see in a particular reactor we can see the change of concentration for a given a component. Or we can follow the change of some physical properties of the fluid or of the reactants which we have given. Physical properties like electrical conductivity or refractive index, the change of these properties we can follow in a particular reactor.

We can also follow the change in total pressure at a constant volume system that means if the reactions happen in gas phase, we can see the change of partial pressure of a particular component at constant volume systems. Or we can also see the change in volume in the system if we keep the pressure constant, so this way these four methods we can follow any type of reactors like batch reactors or flow reactors whatever may be the reactor we choose but we can see this property change with time.

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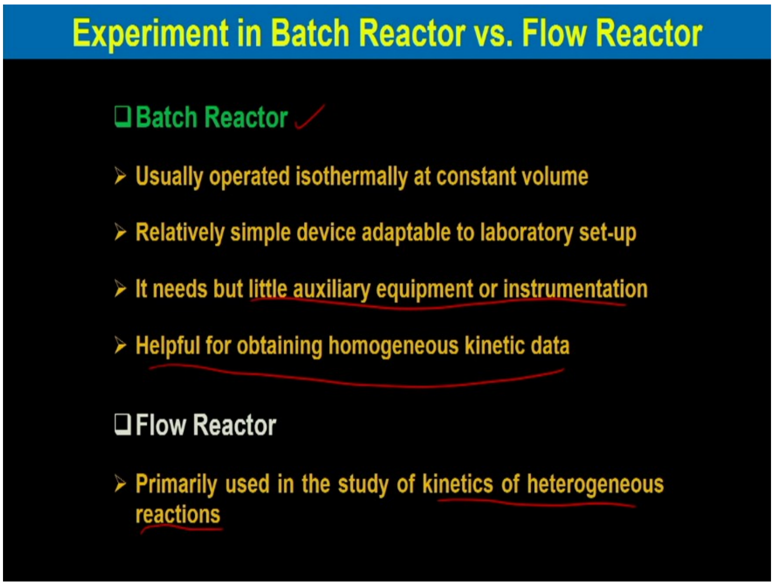

Experiment in Batch Reactor vs. Flow Reactor

❑ Batch Reactor ✓

- Usually operated isothermally at constant volume
- Relatively simple device adaptable to laboratory set-up
- It needs but little auxiliary equipment or instrumentation
- Helpful for obtaining homogeneous kinetic data

❑ Flow Reactor

- Primarily used in the study of kinetics of heterogeneous reactions

Now between these 2 reactors; batch reactors and flow reactors which one we should use for doing the Kinetic analysis? If you consider batch reactor it is usually operated at isothermal conditions at constant volume, and it is very simple device and it can be adaptable to any laboratory setup. It needs but little auxiliary equipment or instrumentation, so very little auxiliary equipment we can perform the batch Reactor Kinetic experiments, very simple operation and it is helpful for homogeneous Kinetic data.

So if our system is homogeneous that means if we have more than one reactants, if they react together in a homogeneous solvent then this batch reactor is helpful to obtain the kinetic data. So generally in most of the homogeneous Kinetic data experiments we perform using the batch reactor.

For flow reactor this is generally used to study the kinetics of the heterogeneous reactions, so which we will discuss in the later part or it may be covered in case of your, you know Chemical Reaction Engineering II where most of the catalytic and heterogeneous reactions are covered. So for the time being we will consider batch reactor kinetic data analysis.

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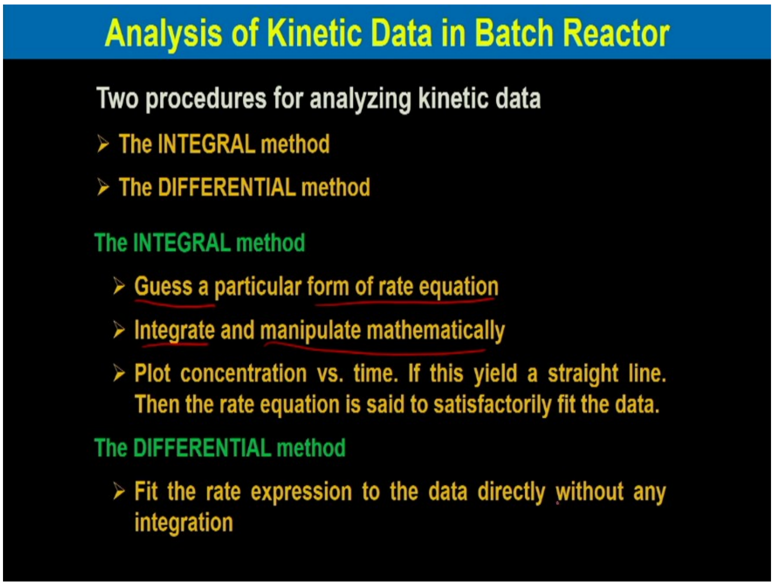

Analysis of Kinetic Data in Batch Reactor

Two procedures for analyzing kinetic data

- The INTEGRAL method
- The DIFFERENTIAL method

The INTEGRAL method

- Guess a particular form of rate equation
- Integrate and manipulate mathematically
- Plot concentration vs. time. If this yield a straight line. Then the rate equation is said to satisfactorily fit the data.

The DIFFERENTIAL method

- Fit the rate expression to the data directly without any integration

To do the batch Reactor Kinetic data analysis, the two procedures we generally use, one is called Integral method, in integral method the other method is the differential method, so these two procedures we generally used to obtain the batch reactor can take data. In integral method what we do, we guess a particular form of rate equation, so first we have to guess a particular form of rate equation.

Then we need to integrate the equation and manipulate mathematically. So if we integrate the rate expression, we generally get the concentration profile that means the concentration versus time, how the concentration in a reactor varying with time so we integrate the rate equations which we guess and then manipulate mathematically.

Now we plot the concentration change versus time, so we plot concentration versus time, if this yields a straight line then the rate equation is said to be satisfactorily fit the data so the rate equation should be a straight line, fit all the kinetic data in a straight line if that is obtained then we can say that the assumed rate expression or guessed rate expression is the correct one.

In case of the differential method what we do, fit the rate expression to the data directly without any integration. So we do not do any integration of the differential form of rate expression because the rate expression is itself a differential form and we take the data directly to fit the differential form of the equation which we do not integrate.

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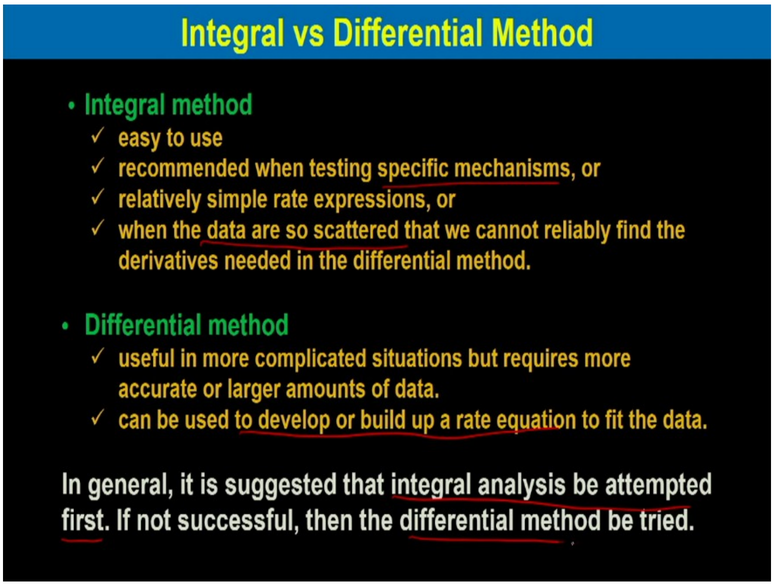

Integral vs Differential Method

- Integral method
  - ✓ easy to use
  - ✓ recommended when testing specific mechanisms, or
  - ✓ relatively simple rate expressions, or
  - ✓ when the data are so scattered that we cannot reliably find the derivatives needed in the differential method.
- Differential method
  - ✓ useful in more complicated situations but requires more accurate or larger amounts of data.
  - ✓ can be used to develop or build up a rate equation to fit the data.

In general, it is suggested that integral analysis be attempted first. If not successful, then the differential method be tried.

Now, between the integral and differential method which one is beneficial and what are their advantages and disadvantages? In case of integral method it is very easy to use because we guess a rate equation and then we integrate it and then we fit the data which we obtain, so it is very easy to use. And recommended for testing specific mechanisms, so we can assume a specific mechanism and according to that we can obtain a general order rate equation and then we test whether it is the mechanism is following as per the guessed kinetics.

It is relatively simple rate expression so or when the data are so scattered that we cannot reliably find the derivatives needed in the differential form. So if the kinetic data are scattered, it may so happen that generally for kinetic experiments there are large deviation from getting the kinetic data because it depends on the reactants and depends on the rate of the chemical reaction, if the reaction is very fast it changes within a period of time, change of the concentration which is happened within a stipulated period of time, we may not get the exact kinetics and the change may not get properly so the data generally scattered. So in that case the derivative method or the differential method we cannot use, in that case the integral method becomes more easy to apply.

In case of differential method it is more useful for complicated situations and requires more accurate or larger amounts of data. So, if we have large amount of data and data are not scattered, the data are very accurate in that case more complicated situations we can handle with differential method. It can be used to develop or build up a rate equation to fit the data so we can use the differential method to develop or build up a rate equation to fit the data. Whereas, in integral method we have to guess the rate equation, but in case of differential method we can develop the rate equation. So the general practice among these 2 methods, in general it is suggested that the integral method of analysis be attempted first. If the integral method is not successful then we will use the differential method, so this is the general procedure to be followed to obtain any rate expression.

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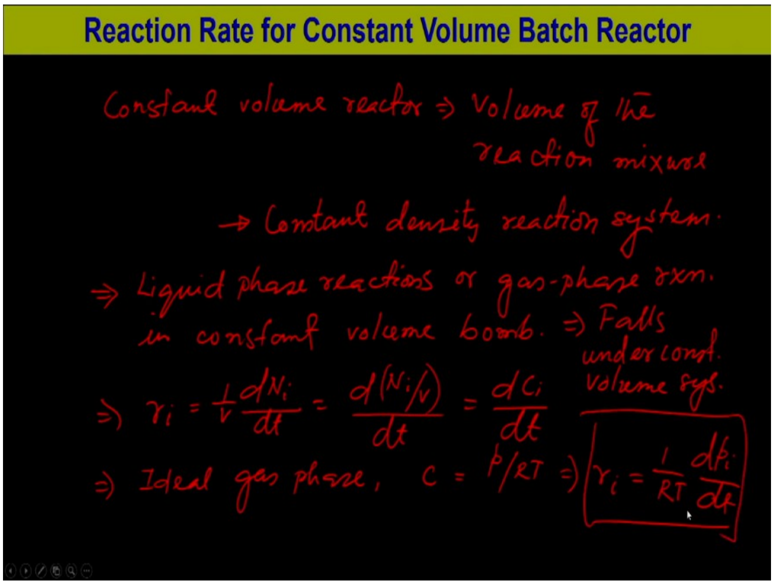

Reaction Rate for Constant Volume Batch Reactor

Constant volume reactor ⇒ Volume of the reaction mixure

→ Constant density reaction system.

⇒ Liquid phase reactions or gas-phase rxn. in constant volume bomb. ⇒ Falls under const. volume sys.

$$\Rightarrow r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt}$$

$$\Rightarrow \text{Ideal gas phase, } C = p/RT \Rightarrow \boxed{r_i = \frac{1}{RT}\frac{dp_i}{dt}}$$

Now, reaction rate for constant volume batch reactor. So when we talk on constant volume batch reactor, it means that the volume of the reactant not the volume of the reactor. So the amount of volume, the amount of reactants and its volume represents the volume of the batch reactor, but it is not the volume of the reactor so this essentially refers to the constant density reaction system.

Constant volume reactor means volume of the reaction mixture and this actually represents the constant density reaction system. Most of the liquid phase reaction or if the reaction of the gas phase is happening in a constant volume batch so gas phase reaction in constant volume batch constant volume bomb, these all falls under constant volume system.

Now for a constant volume reactant i which is happening in a constant volume reactor we can write the rate of reaction,

$$r_i = \frac{1}{V}\frac{dN_i}{dt}$$

which is equal to

$$= \frac{d(N_i / V)}{dt}$$

because since volume is constant so this we can represent as $\frac{dC_i}{dt}$. Now if the reaction is happening in the gas phase and the gas phase is ideal, we can write the concentration term C for ideal gas phase C would be equal to $\frac{p}{RT}$ that means p is the partial pressure of that component. So we can write this expression,

$$r_i = \frac{1}{RT}\frac{dp_i}{dt}$$

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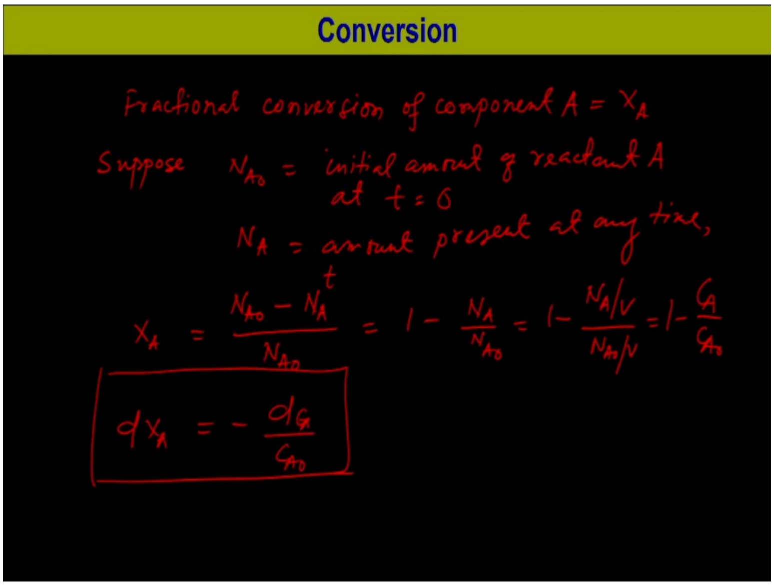

Conversion

Fractional conversion of component A = X_A

Suppose N_{A0} = initial amount of reactant A at t = 0

N_A = amount present at any time, t

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}} = 1 - \frac{N_A/V}{N_{A0}/V} = 1 - \frac{C_A}{C_{A0}}$$

$$\boxed{dX_A = -\frac{dC_A}{C_{A0}}}$$

Now, let us introduce another term which is conversion, the conversion or the fractional conversion of any reactant say A can be represented with a symbol fractional conversion of component A can be represented with X_A or we simply call the conversion of A. Now suppose, we had initially N_{A0} moleS of component A so N_A is the initial amount of reactant A at time t = 0 and N_A is the amount present at any time t. So we can write the conversion for a constant volume system that is X_A would be the

$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

so this we can write

$$X_A = 1 - \frac{N_A}{N_{A0}}$$

Now, if we just divide the numerator and denominator here by V for constant volume system, we can write

$$1 - \frac{N_A / V}{N_{A0} / V}$$

so we can write

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

Now, if we differentiate this equation we will have relation between X_A, dX_A with dC_A. So we can write

$$dX_A = -\frac{dC_A}{C_{A0}}$$

So this is the relation in terms of the differential form of fractional conversion with the change in concentration.

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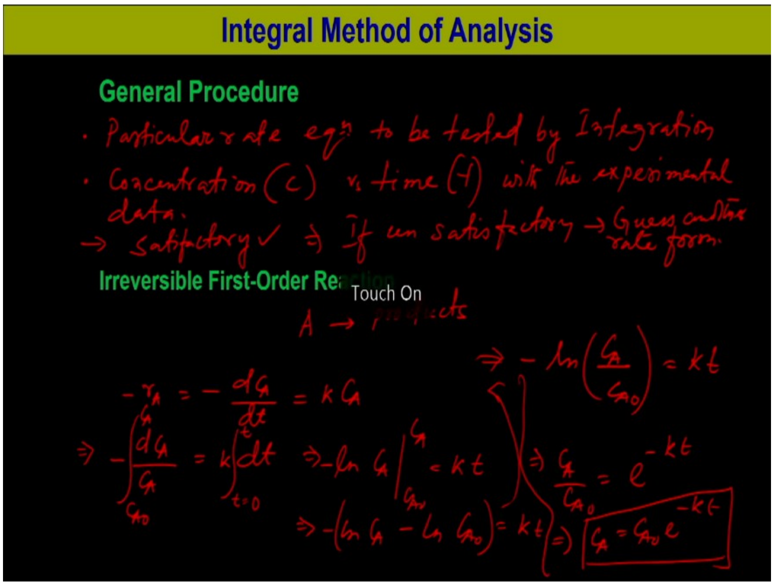

Integral Method of Analysis

General Procedure

- Particular rate eqn to be tested by Integration
- Concentration (c) vs time (t) with the experimental data.

→ satisfactory ✓ ⇒ If unsatisfactory → Guess another rate form.

Irreversible First-Order Re

Touch On

$A \to \text{products}$

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

$\Rightarrow -\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_{t=0}^{t} dt \Rightarrow -\ln C_A \Big|_{C_{A0}}^{C_A} = kt$

$\Rightarrow -(\ln C_A - \ln C_{A0}) = kt$

$\Rightarrow -\ln\left(\frac{C_A}{C_{A0}}\right) = kt \Rightarrow \frac{C_A}{C_{A0}} = e^{-kt} \Rightarrow \boxed{C_A = C_{A0}e^{-kt}}$

Now, integral method of analysis, the general procedure as we have said for any integral method of analysis, what we need to do? First we need to get the particular form of rate expression, so we have to get particular rate equation which is to be tested by integration so we assume a particular rate equation that will be integrated in a particular form and then the second step is to plot concentration versus time, and that would be with the experimental data.

So if you do so, if the fit which we have done with this, if this is satisfactory then we will get the appropriate rate equations and if it is unsatisfactory then guess another rate form and then similar procedure would be followed, so this is the general procedure.

Next we will consider the unimolecular first order reactions, irreversible first order reactions. Let us consider a general reaction which is

$$A \to products$$

Now, if the as we said this is first order reaction so the rate equations we can write

$$-r_A = -\frac{dC_A}{C_A} = kC_A$$

If we separate the variables from here we can write

$$-\frac{dC_A}{C_A} = kdt$$

Now, if we put the integral for both the cases, it would be from C_{A0} which was the initial concentration to C_A at any time t so initially t = 0 to any time t. So with this limit if we integrate this expression, it will be

$$\left[-\ln C_A\right]_{C_{A0}}^{C_A} = kt$$

So if we substitute this, this would be

$$-(\ln C_A - \ln C_{A0}) = kt$$

and from here we can write

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

so this is in terms of the concentration profile. We can also write

$$\frac{C_A}{C_{A0}} = e^{-kt}$$

we can write

$$C_A = C_{A0}e^{-kt}$$

so this is for concentration profile for first order reaction.

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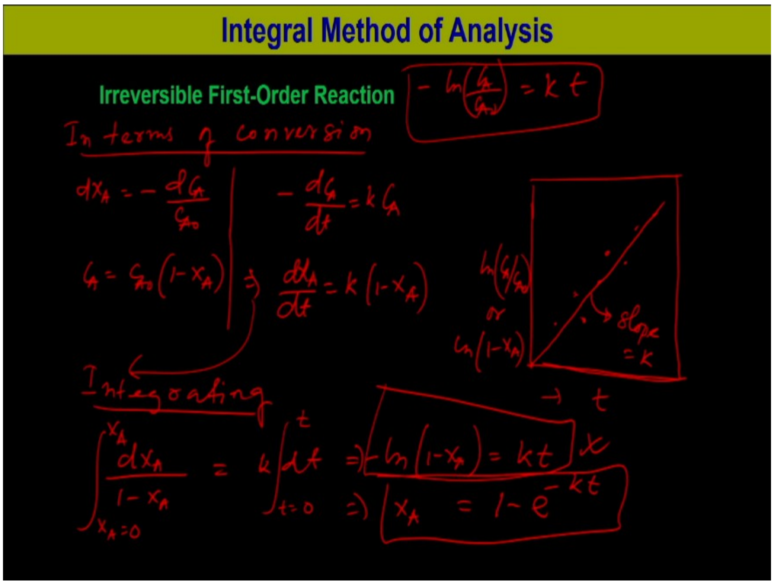

Integral Method of Analysis

Irreversible First-Order Reaction

$$\boxed{-\ln\left(\frac{C_A}{C_{A0}}\right) = kt}$$

In terms of conversion

$$dX_A = -\frac{dC_A}{C_{A0}} \qquad -\frac{dC_A}{dt} = kC_A$$

$$C_A = C_{A0}(1-X_A) \Rightarrow \frac{dX_A}{dt} = k(1-X_A)$$

Integrating

$$\int_{X_A=0}^{X_A}\frac{dX_A}{1-X_A} = k\int_{t=0}^{t}dt \Rightarrow \boxed{-\ln(1-X_A) = kt}$$

$$\Rightarrow \boxed{X_A = 1-e^{-kt}}$$

Now this expression we can write in terms of the conversion. So in terms of conversion we can write as we have seen earlier that

$$dX_A = -\frac{dC_A}{C_{A0}}$$

So if we substitute in the rate expression that is

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

we can write

$$C_A = C_{A0}(1 - X_A)$$

we can write this expression as

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

Now, if we integrate this expression, we would obtain so by separation of the variables we can write

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

Now, if we integrate with a limit when t=0, the conversion is X_A=0, and when t=t the conversion is X_A.

$$\int_{X_A=0}^{X_A} \frac{dX_A}{(1 - X_A)} = k\int_{t=0}^{t} dt$$

So if we integrate this, this would be

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

So from here we can write,

$$X_A = 1 - e^{-kt}$$

So this is in terms of the conversion so we can write both in terms of the concentration or in terms of the conversion.

Now, if we plot say this Y axis is time and X axis we can plot $\ln\frac{C_A}{C_{A0}}$ or $\ln(1-X_A)$, so we have two expressions; one is this one, another one is

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

So if you plot $\ln\frac{C_A}{C_{A0}}$ verses t in this expression as you can see, it will lead to a straight line with a slope k. Similarly, from this expression if we plot $\ln(1-X_A)$ versus t, we will get a straight line. So if we have the rate data obtained from the batch reactor we can fit the data and it will lead to a straight line passing through the origin with a slope is equal to k. So if the data fits in a linear curve straight line then the kinetics of which we guessed as a first order kinetics will be obtained.

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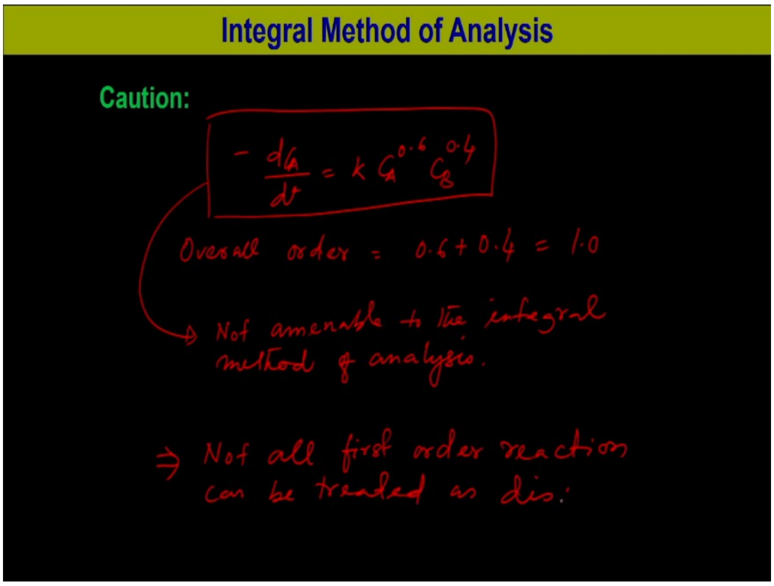

Integral Method of Analysis

Caution:

$$\boxed{-\frac{dC_A}{dt} = k\,C_A^{0.6}\,C_B^{0.4}}$$

Overall order = $0.6 + 0.4 = 1.0$

→ Not amenable to the integral method of analysis.

⇒ Not all first order reaction can be treated as this.

But if we look into the rate expression, although it is first order but in different forms. Suppose, if the rate expression is like this,

$$-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$$

So as you can see, the overall order of the reaction is 1 so this is also first-order reaction, so overall order for this rate expression is

$$0.6 + 0.4 = 1,$$

So although this rate expression is of the first order in nature, but it is not amenable for the solution using integral method, is not amenable to the integral method of analysis. So the caution over here is that not all first-order reactions can be treated as integral method as explained before, so not all first order reactions can be treated as discussed.

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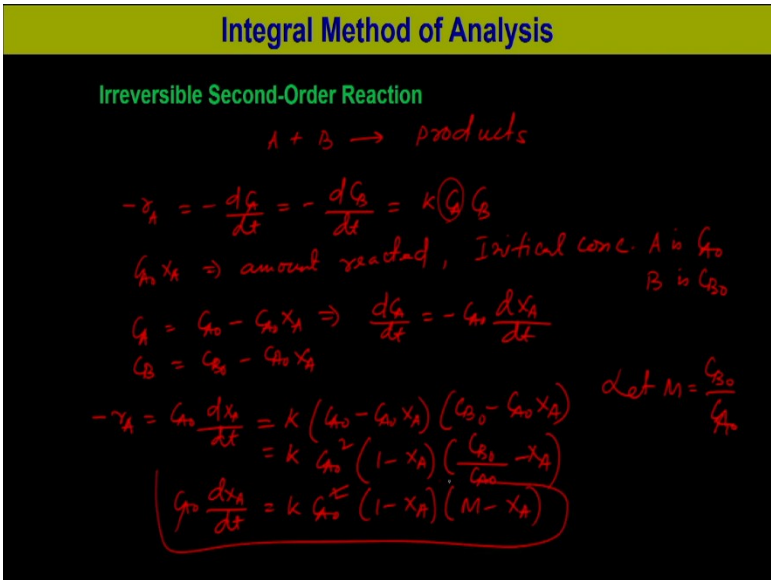

Integral Method of Analysis

Irreversible Second-Order Reaction

$$A + B \rightarrow products$$

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k C_A C_B$$

$C_{A0}X_A \Rightarrow$ amount reacted, Initial conc. A is C_{A0}
B is C_{B0}

$$C_A = C_{A0} - C_{A0}X_A \Rightarrow \frac{dC_A}{dt} = -C_{A0}\frac{dX_A}{dt}$$

$$C_B = C_{B0} - C_{A0}X_A$$

Let $M = \frac{C_{B0}}{C_{A0}}$

$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

$$= k\,C_{A0}^2(1-X_A)\left(\frac{C_{B0}}{C_{A0}} - X_A\right)$$

$$\boxed{C_{A0}\frac{dX_A}{dt} = k\,C_{A0}^{\cancel{2}}(1-X_A)(M-X_A)}$$

Now, let us consider second order kinetics, irreversible second order reactions. So if the reaction is second order, let us consider the general reactions which is

$$A + B \rightarrow products$$

If we write the rate expression for the second order reactions, we can write

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B$$

Now, the conversion if we consider X_A for component A the amount of A which will be reacted is $C_{A0}X_A$, so this is the amount reacted. And let the initial concentration of A and B; A is C_{A0} and B is C_{B0}, so we can write the concentration at any time t C_A would be

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

and C_B would be

$$C_B = C_{B0} - C_{A0}X_A$$

Now if we substitute in this rate expression, we can obtained

$$-r_A = C_{A0}\frac{dX_A}{dt}$$

How we obtained $\frac{dX_A}{dt}$? If we differentiate this expression, $C_A = C_{A0} - C_{A0}X_A$ it would be

$$\frac{dC_A}{dt} = -C_{A0}\frac{dX_A}{dt}$$

So if we substitute here,

$$-C_{A0}\frac{dX_A}{dt}$$

in this expression, it would be

$$C_{A0}\frac{dX_A}{dt} = kC_A$$

In this expression C_A would be

$$C_A = (C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

So then we will obtain

$$C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

Now let

$$M = \frac{C_{B0}}{C_{A0}}$$

so if we assume that $M = \frac{C_{B0}}{C_{A0}}$, we can write this expression as

$$kC_{A0}^2(1 - X_A)(M - X_A)$$

So from here C_{A0} out so you will have

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(M - X_A)$$

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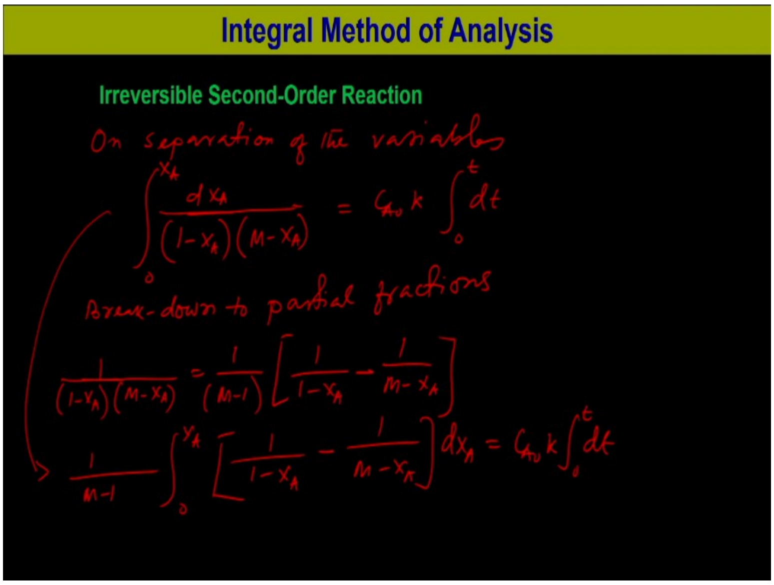

Integral Method of Analysis

Irreversible Second-Order Reaction

On separation of the variables

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0} k \int_0^t dt$$

Break-down to partial fractions

$$\frac{1}{(1-X_A)(M-X_A)} = \frac{1}{(M-1)}\left[\frac{1}{1-X_A} - \frac{1}{M-X_A}\right]$$

$$\frac{1}{M-1}\int_0^{X_A}\left[\frac{1}{1-X_A} - \frac{1}{M-X_A}\right] dX_A = C_{A0} k \int_0^t dt$$

Now, if we do the separation of the variables of this expression, so on separation of the variables we will obtain the

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = kC_{A0}\int_0^t dt$$

Now we have to break down into partial fractions of the left-hand side, so breakdown to partial fractions. So to do that we can write this

$$\frac{X_A}{(1-X_A)(M-X_A)} = \frac{1}{(M-1)}\left[\frac{1}{1-X_A} - \frac{1}{M-X_A}\right]$$

Now, if we substitute this over here and then we do integration, we will obtain from here we can write

$$\frac{1}{(M-1)}\int_0^{X_A}\left[\frac{1}{1-X_A} - \frac{1}{M-X_A}\right]dX_A = kC_{A0}\int_0^t dt$$

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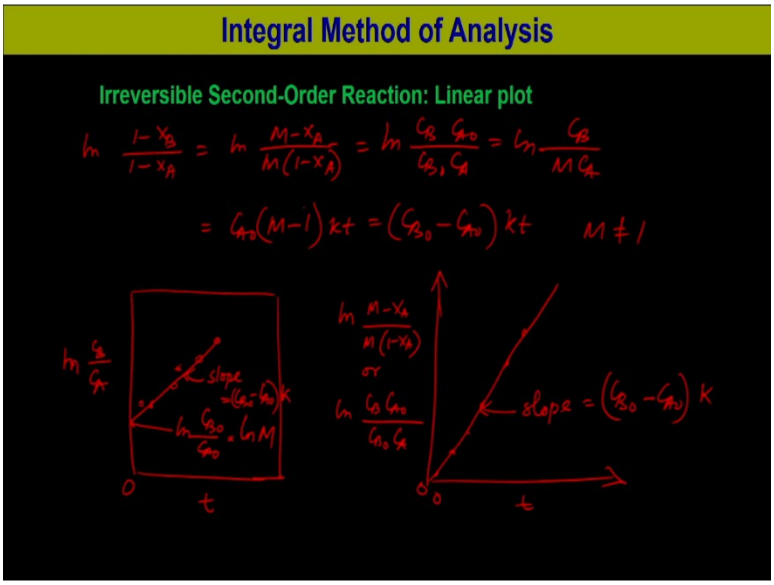

Integral Method of Analysis

Irreversible Second-Order Reaction: Linear plot

$$\ln\frac{1-X_B}{1-X_A} = \ln\frac{M-X_A}{M(1-X_A)} = \ln\frac{C_B C_{A0}}{C_{B0} C_A} = \ln\frac{C_B}{M C_A}$$

$$= C_{A0}(M-1)kt = (C_{B0}-C_{A0})kt \quad M \neq 1$$

Now if we integrate this expression, this will take the form

$$\ln\frac{1-X_B}{1-X_A} = \ln\frac{M-X_A}{M(1-X_A)} = \ln\frac{C_B C_{A0}}{C_{B0} C_A} = \ln\frac{C_B}{M C_A}$$

which is equal to

$$= C_{A0}(M-1)kt = (C_{B0}-C_{A0})kt$$

So that this equation as you can see this is only valid when $M \neq 1$, so when M = 1 this is undefined so this equation cannot be valid.

Now, if we plot the concentration versus time, so we will obtain this is $\ln\frac{C_B}{C_A}$ versus time, so if we plot then we will obtain this is 0, we will obtain a curve like this which is so the intersect here is $\ln\frac{C_{B0}}{C_{A0}} = \ln M$ and the slope of this curve would be equal to $(C_{B0}-C_{A0})k$. If we plot like this similarly, this is time and this is $\ln\frac{M-X_A}{M(1-X_A)}$ or we can plot $\ln\frac{C_B C_{A0}}{C_{B0} C_A}$. So if we plot then we can obtain a curve which is passing through the origin, it is a straight line with a slope is equal to $(C_{B0}-C_{A0})k$.

So this way we can interpret the second order rate expression by integral method, and if the concentration of component B is such that the change of concentration due to the reaction of A and B, the change of concentration of B is negligible that means the component B is present in large excess, so its concentration does not change much so in that case this equation will reduce to the pseudo first order reaction.

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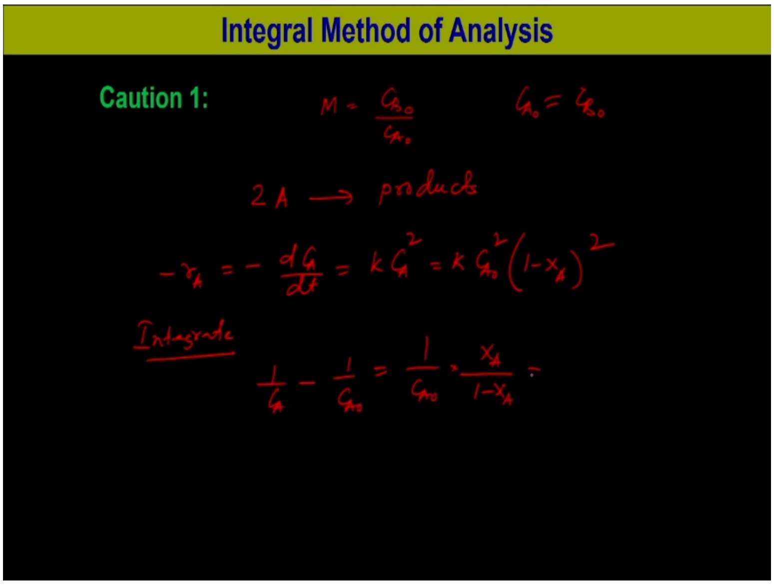

Integral Method of Analysis

Caution 1:

$M = \frac{C_{B0}}{C_{A0}}$ $C_{A0} = C_{B0}$

$2A \longrightarrow products$

$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1-X_A)^2$

Integrate

$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} * \frac{X_A}{1-X_A} =$

Let us consider two different cautions; one is, if the reactant introduced in equivalent amount so equimolar or stoichiometry amount. So in that case $M = \frac{C_{B0}}{C_{A0}}$, if $C_{A0} = C_{B0}$ that is stoichiometry amount then M = 1 and then the treatment which we have done before is not valid. Or if the reaction in two moles of A reacting and producing some product will be treated in a different way. Like if we have

$$2A \rightarrow products$$

in that case we will get the rate expression is

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

Now, if we integrate this expression then we will obtain

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

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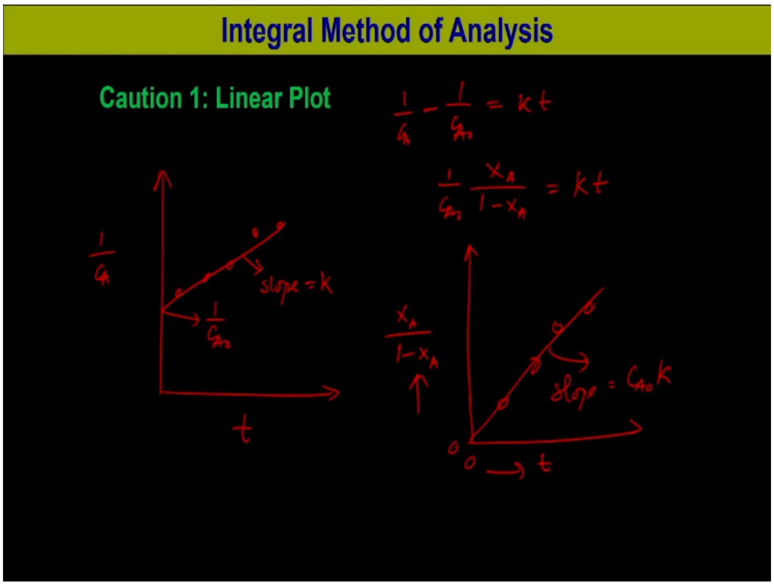

Integral Method of Analysis

Caution 1: Linear Plot

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

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

Now, if we plot this expression so we would obtain a curve like this. So $\frac{1}{C_A}$ versus time if we plot for the equation

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

so in that case we will obtain a straight line passing through some point on the Y axis. So this means this is your intersect which is $\frac{1}{C_{A0}}$, and the slope of the curve is k.

Or if we plot the other part that is

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

so in terms of conversion if we plot, this would give t and this part is $\frac{X_A}{1-X_A}$, so we will obtain a curve which is passing through the origin with a slope so the slope of the curve would be kC_{A0}. So when we have a second order reactions and the reactants are in introduced in stoichiometric amount we have to treat differently.

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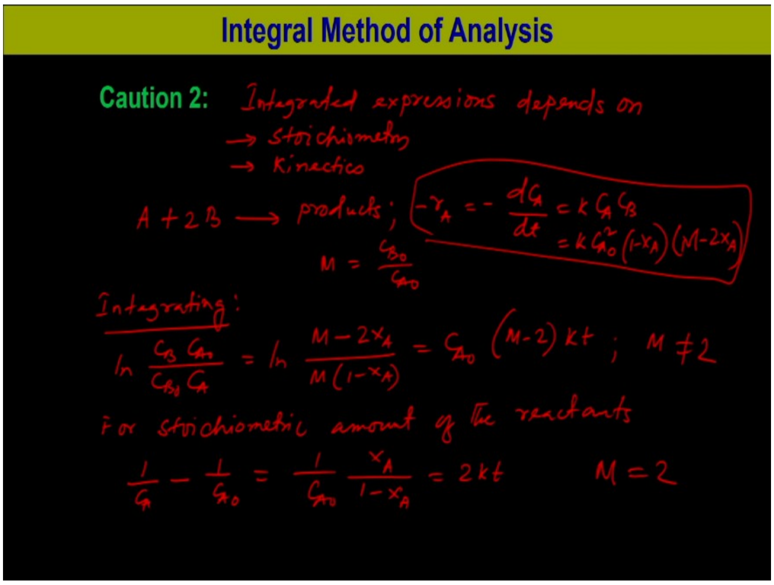

Integral Method of Analysis

Caution 2: Integrated expressions depends on

→ stoichiometry

→ Kinectics

$A + 2B \longrightarrow$ products ; $\boxed{-r_A = -\frac{dC_A}{dt} = kC_A C_B = kC_{A0}^2(1-X_A)(M-2X_A)}$

$M = \frac{C_{B0}}{C_{A0}}$

Integrating:

$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{M-2X_A}{M(1-X_A)} = C_{A0}(M-2)kt \; ; \; M \neq 2$

For stoichiometric amount of the reactants

$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1-X_A} = 2kt \qquad M = 2$

Now, another caution for this type of analysis is that the kinetics of the reaction or the reaction kinetics as well as the stoichiometry how that influence the analyses of the integral methods. So integrated expression depends on both, the stoichiometry as well as the kinetics. Let us take an example,

$$A + 2B \rightarrow products$$

so this reaction if we assume this is second order that is it is first order with respect to A and first order with respect to B and overall second order reaction then we can write the rate of reaction

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

and which we can write

$$= kC_{A0}^2(1 - X_A)(M - 2X_A)$$

here $M = \frac{C_{B0}}{C_{A0}}$.

Now, if we integrate this rate expression, we would obtain

$$\ln\frac{C_B C_{A0}}{C_{B0} C_A} = \ln\frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt$$

and this equation would be valid when $M \neq 2$, so if it is M is equal to 2 this is not valid.

So when we incorporate stoichiometric amount of the reactants, in that case the integrated form for stoichiometric amount of the reactants, the integrated form would be

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt$$

So this is valid when M = 2. So both from here we can see that both stoichiometry and the reaction kinetics that is it is for non-elementary reactions. The reactions

$$A + 2B \rightarrow products$$

which is considered as non-elementary reactions because we have considered as second order reaction.

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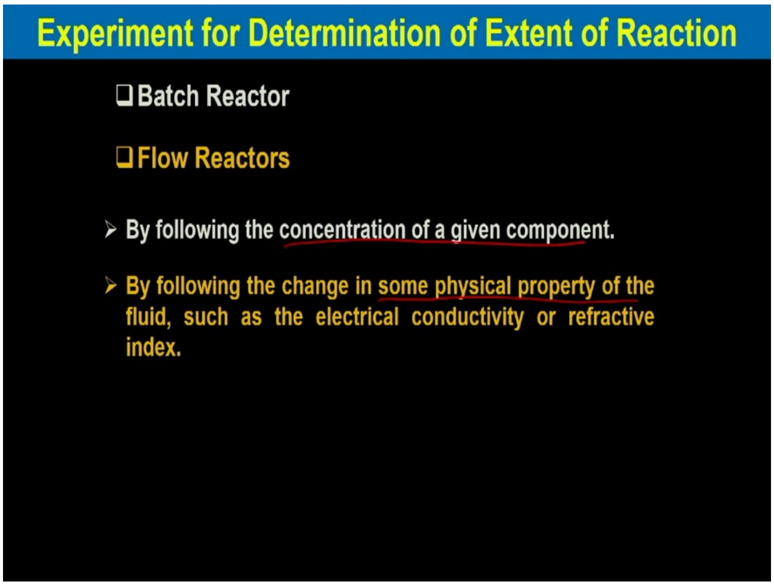

Experiment for Determination of Extent of Reaction

- ☐ Batch Reactor
- ☐ Flow Reactors

- ➢ By following the concentration of a given component.
- ➢ By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.

Now, if we consider irreversible Third order reactions, let us take an example. Say the reaction is A plus B plus D producing products. So the rate equations we can write for the third order reactions is

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B C_D$$

Now in terms of conversion we can write

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}^3(1 - X_A)(\frac{C_{B0}}{C_{A0}} - X_A)(\frac{C_{D0}}{C_{A0}} - X_A)$$

Now, if we take this equation differential equation and if we separate the variables and breakdown into partial fractions then with integration and manipulation we can obtain so separation of variables then breakdown to partial fractions and integration, this will lead to

$$\frac{1}{(C_{A0}-C_{B0})(C_{A0}-C_{D0})}\ln\frac{C_{A0}}{C_A}+\frac{1}{(C_{B0}-C_{D0})(C_{B0}-C_{A0})}\ln\frac{C_{B0}}{C_B}+\frac{1}{(C_{D0}-C_{A0})(C_{D0}-C_{B0})}\ln\frac{C_{D0}}{C_D}=kt$$

So this is the integral form of third order reaction as shown above.

Now, if we consider any one component in large access, the same equation will reduce to the second order reaction so which we can compare with the derivations we have done, integral form of the rate equation we have derived earlier for the second order reaction.

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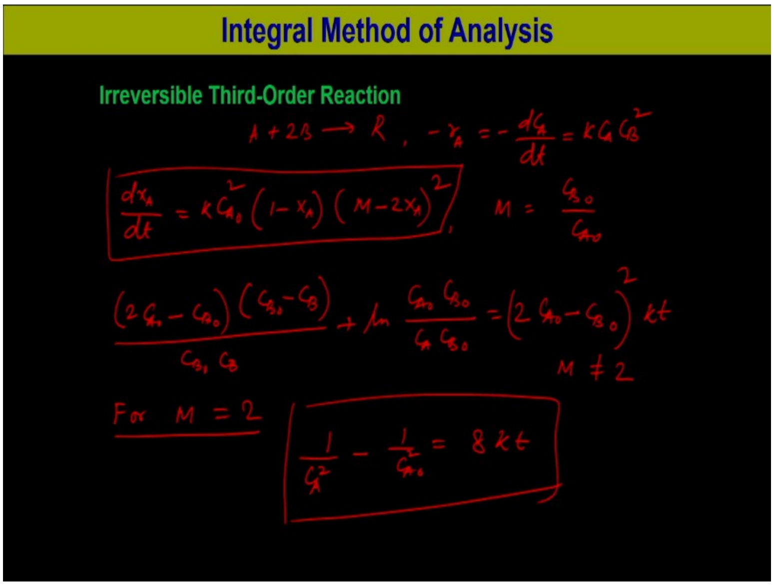

Integral Method of Analysis

Irreversible Third-Order Reaction

$A + 2B \rightarrow R$, $-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$

$\boxed{\frac{dX_A}{dt} = kC_{A0}^2(1-X_A)(M-2X_A)^2}$, $M = \frac{C_{B0}}{C_{A0}}$

$$\frac{(2C_{A0}-C_{B0})(C_{B0}-C_B)}{C_{B0}C_B} + \ln\frac{C_{A0}C_{B0}}{C_A C_{B0}} = (2C_{A0}-C_{B0})^2 kt$$

$M \neq 2$

For $M = 2$

$$\boxed{\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 8kt}$$

Now another example of third order reaction is

$$A + 2B \rightarrow R$$

with rate of reactions

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$$

Now same thing we can write in terms of conversion which is

$$\frac{dX_A}{dt} = kC_{A0}^2(1-X_A)(M-X_A)^2$$

Now if we consider, so here $M = \frac{C_{B0}}{C_{A0}}$.

Now if we integrate this relation we will obtain

$$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln\frac{C_B C_{A0}}{C_{B0}C_A} = (2C_{A0} - C_{B0})^2 kt$$

so this equation is valid when $M \neq 2$. Now for M = 2 if we integrate from here for the third order reactions then in that case we will obtain

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 8kt$$

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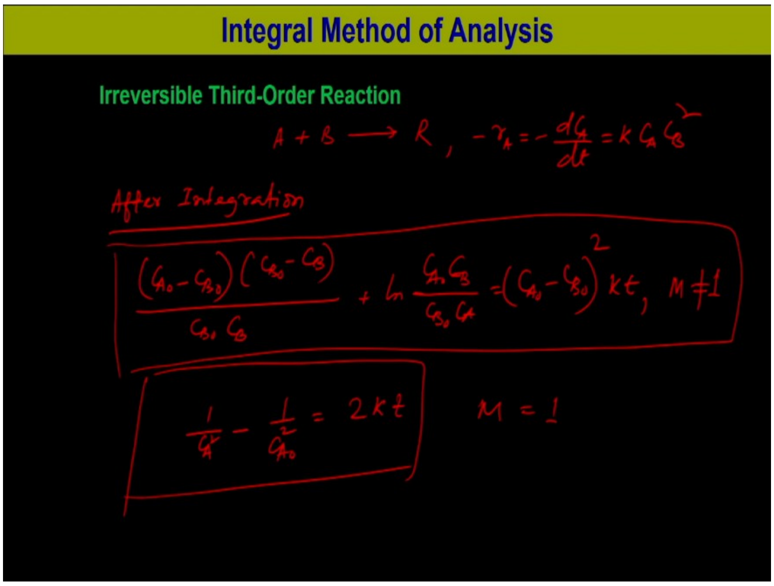

Integral Method of Analysis

Irreversible Third-Order Reaction

$A + B \longrightarrow R$, $-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$

After Integration

$$\boxed{\frac{(C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln\frac{C_{A0}C_B}{C_{B0}C_A} = (C_{A0} - C_{B0})^2 kt, \quad M \neq 1}$$

$$\boxed{\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2kt} \qquad M = 1$$

Now similarly, if we consider the another reaction of third order which is

$$A + B \rightarrow R$$

So this is non-elementary reaction and of third order where 1 mole of A is reacting 1 mole of B producing R, this reaction is considered as third order reaction. So in that case the rate of reaction if we write

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$$

Now if we integrate this equation like earlier, we would obtain

$$\frac{(C_{A0}-C_{B0})(C_{B0}-C_B)}{C_{B0}C_B}+\ln\frac{C_BC_{A0}}{C_{B0}C_A}=(C_{A0}-C_{B0})^2 kt$$

So this equation is valid when $M \neq 1$. Now for M = 1 we can get for third order reactions

$$\frac{1}{C_A^2}-\frac{1}{C_{A0}^2}=2kt$$

So these are the two integral forms of the rate equation for third order reactions with different stoichiometric ratio, which is not equal to 1 and one is the stoichiometry ratio is 1.

So overall we can see that the stoichiometry and kinetics of the reactions are both important to represent the integral form of the rate equations and analysing the data from the batch reactor analysis. So thank you very much for attending this lecture, and we will continue our discussion on the batch reactor data in the next class as well.