Chemical Reaction Engineering I
Professor Bishnupada Mandal
Department of Chemical Engineering
Indian Institute of Technology Guwahati
Lecture 10
Differential Method of Analysis and Variable Volume Batch Reactor Data

Welcome to the fourth lecture of module three, in this module we are discussing analysis of the batch reactor kinetic data. In the last three lectures we have mostly covered the analysis of the batch reactor data by Integral method of analysis and the volume of the reactor we have considered constant volume.

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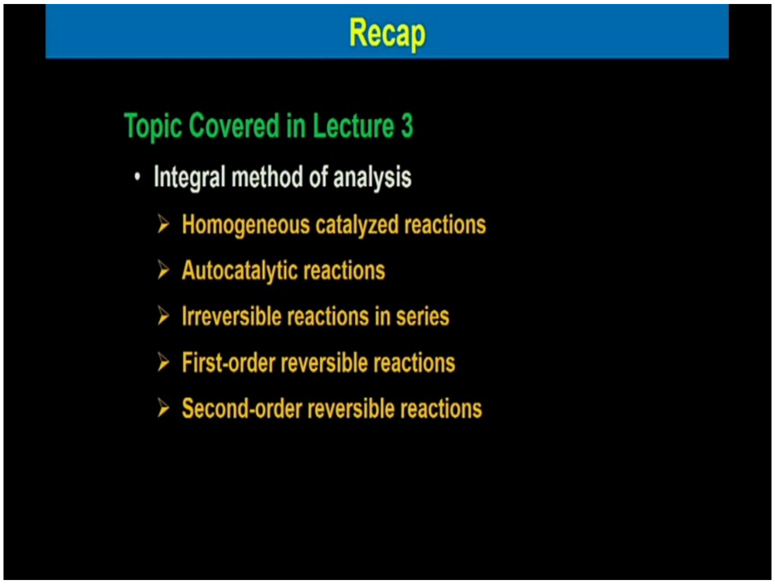

Recap

Topic Covered in Lecture 3

- Integral method of analysis
  - Homogeneous catalyzed reactions
  - Autocatalytic reactions
  - Irreversible reactions in series
  - First-order reversible reactions
  - Second-order reversible reactions

Let us have a brief recap of our last lecture we had, in the last lecture we discussed Homogeneous catalyzed reactions, then we have discussed Autocatalytic reactions. So for the homogeneous catalyzed reactions we have seen that we need to have some catalyst which will give the product or enhance the rate of the chemical reactions but at the same time the reactants itself can convert to the products without any catalysts, so the reaction proceeds in two pathways. So this is called parallel reactions; conversion of a certain component through non catalytic and catalytic reactions and that we have discussed under homogeneous catalyzed reactions.

In Autocatalytic reactions that means one of the products is reacting with the reactants to produce products. So this is called autocatalytic reactions and to start the autocatalytic reactions some of the products must be present at the beginning to start the reaction. Then we have discussed Irreversible reactions in series, series reactions. Then First-order reversible reactions and Second-order reversible reactions and we have concluded that any reactions more than second-order is very difficult to treat analytically.

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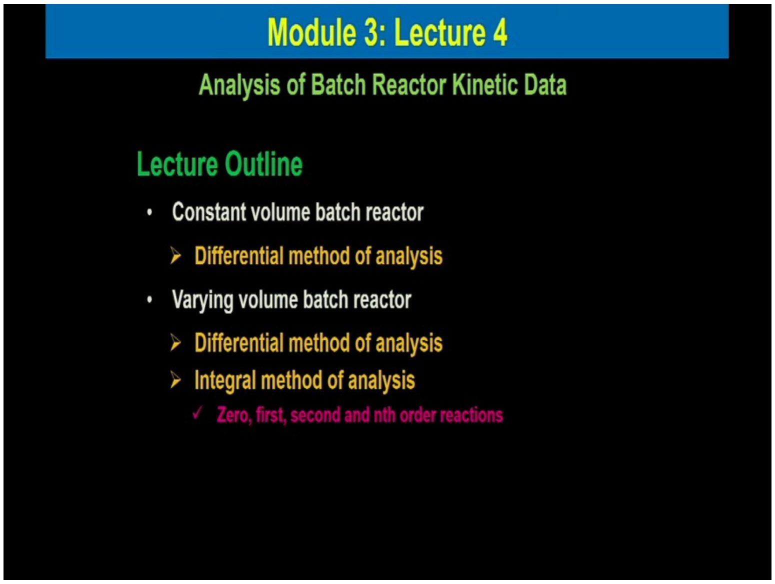

Module 3: Lecture 4

Analysis of Batch Reactor Kinetic Data

Lecture Outline

- Constant volume batch reactor
  - Differential method of analysis
- Varying volume batch reactor
  - Differential method of analysis
  - Integral method of analysis
    - ✓ Zero, first, second and nth order reactions

So in this lecture we will consider Constant volume batch reactor data analysis and that is Differential method of analysis, then we will consider Varying volume batch reactor and that also we will analyze by differential method of analysis as well as the integral method of analysis. So under Integral method of analysis we will mostly consider zero order, first order, second order and nth order reactions.

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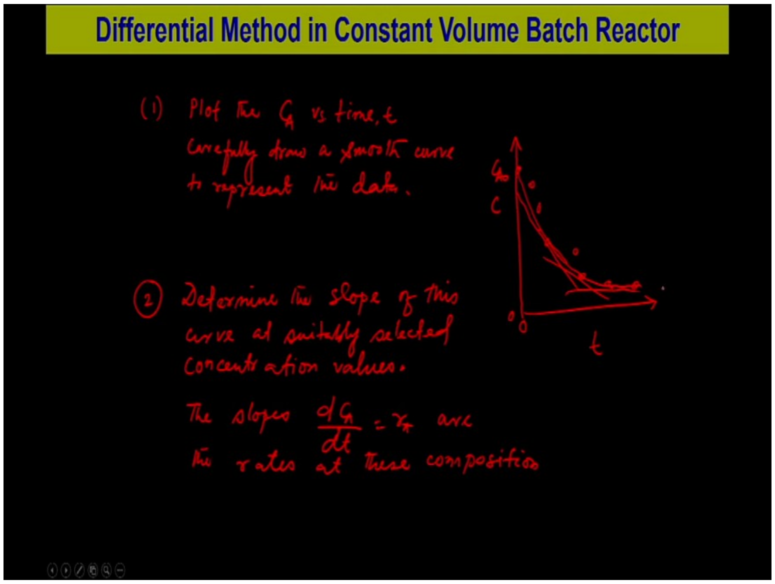

Differential Method in Constant Volume Batch Reactor

(1) Plot the C_A vs time, t
Carefully draw a smooth curve
to represent the data.

② Determine the slope of this
curve at suitably selected
concentration values.

The slopes $\frac{dC_A}{dt} = r_A$ are
the rates at these composition

So let us start with Constant volume batch reactor with differential method of analysis. As we said at the beginning in case of the differential method of analysis we directly take the differential form of the rate equations and test it whether it fitted the desired data obtained from the batch reactor. The methods of the fitting generally follows three steps, in step 1 we plot the concentration of a component versus time t.

So if we plot concentration versus time and we start with the concentration, say C_{A0} naught and we calculate the concentration at different time. So if we plot the concentration versus time data which we have given over here, then carefully draw a smooth curve to represent the data. So with the eye as a guide we can plot the data smooth curve joining the points and as you can see the data, all data may not pass through all the points. So this is how we will follow step 1.

And then in step 2, determine the slope of this curve at suitably selected concentration values. Then the (slope) slopes which is

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

are the rates at these composition. So we have to select at different locations points and we have to draw tangents to calculate the slope and so on.

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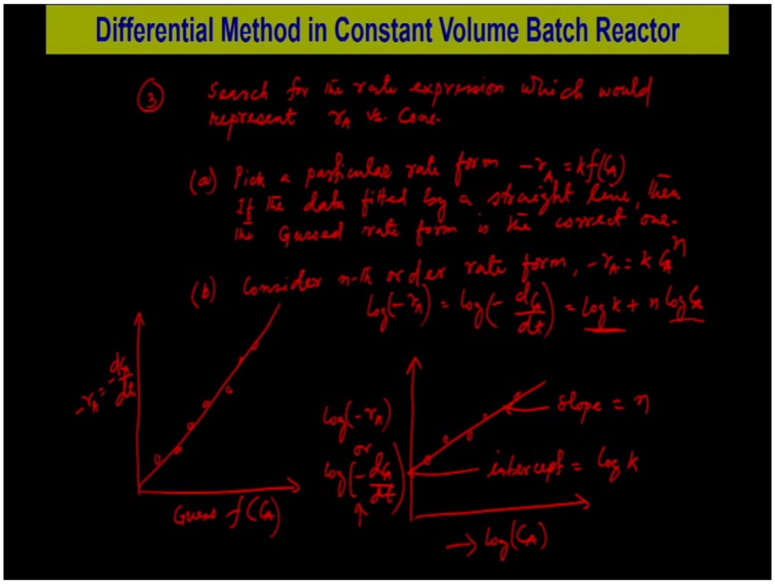

Differential Method in Constant Volume Batch Reactor

③ Search for the rate expression which would represent r_A vs. Conc.

(a) Pick a particular rate form $-r_A = kf(C_A)$
If the data fitted by a straight line, then the Guessed rate form is the correct one.

(b) Consider n-th order rate form, $-r_A = kC_A^n$
$\log(-r_A) = \log\left(-\frac{dC_A}{dt}\right) = \log k + n\log C_A$

Now, next step would be, we need to search for the rate expression which would represent the rate versus concentration data that can be done. So our search would be, search for the rate expression which would represent r_A versus concentration. So this can be done two ways, one we can pick a particular rate form, pick a particular rate form that means $-r_A$ is a function of concentration into k, so

$$-r_A = kf(C_A)$$

k is the rate coefficient and we can plot like this as we have done for integral method of analysis.

Similarly, here we will take the

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

versus we considered a guess kinetics which is function of concentration say first order, second order, third order whatever may be the kinetics we can consider here and we can plot the data and if it is fitted with a straight line passing through the origin then the guessed kinetics is fine. So if the data fitted by a straight line, then the guessed kinetics rate form is the correct one.

Now second way of testing the rate form, let us consider nth order form, consider nth order rate form say that is

$$-r_A = kC_A^n$$

And we can take logarithmic of this one, then we can write

$$\log(-r_A) = \log(-\frac{dC_A}{dt}) = \log k + n \log C_A$$

So now if we plot, $\log(-r_A)$ or $\log(-\frac{dC_A}{dt})$ versus say $\log C_A$. So then we can get a data which is fitted with a straight line, but in this case it will not pass through the origin, so there will be intercept and the intercept is log k. So this intercept is log k and the slope of this will give the order of the reaction n, so from slope of the reaction we can calculate the order of the reaction and then we can calculate the rate form.

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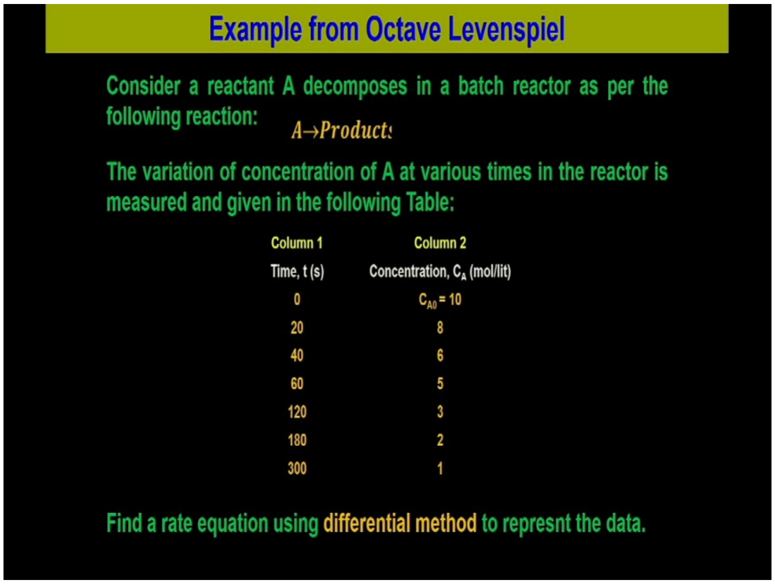

Example from Octave Levenspiel

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:

Column 1	Column 2
Time, t (s)	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 differential method to represnt the data.

So let us take an example, the same example which we have considered for the batch reactor data analysis by integral method. If we consider the same example from the Levenspiel, consider a reactant A decomposes in a batch reactor as per the following reactions,

$$A \rightarrow products$$

and the variation of the concentration of A at various time in the reactor is measured and given in the following table. So this is the table where column 1 represents the time and this is the concentration. Now we need to find the rate equation using differential method of analysis to represent the data. Okay.

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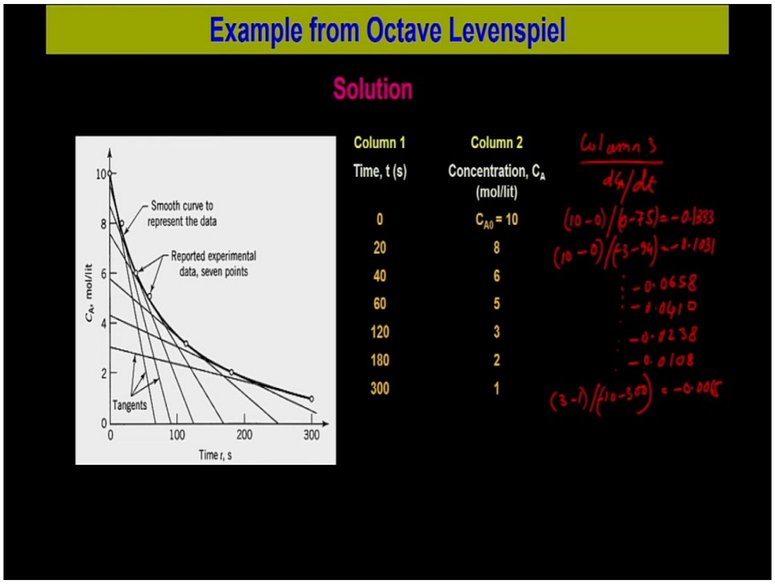

Example from Octave Levenspiel

Solution

Column 1 Time, t (s)	Column 2 Concentration, C_A (mol/lit)	Column 3 dC_A/dt
0	$C_{A0} = 10$	$(10-0)/(0-75) = -0.1333$
20	8	$(10-0)/(-3-94) = -0.1031$
40	6	-0.0658
60	5	-0.0410
120	3	-0.0238
180	2	-0.0108
300	1	$(3-1)/(10-300) = -0.0085$

So if we plot the data concentration versus time we will get the concentration time data as we have seen. So first we have to plot the concentration and time data and we have to draw a smooth curve by hand which is shown over here. Now we have to select different concentrations as we have given, time and concentration. These are the concentration and for each point we can calculate the tangent, if they fall under the smooth curve.

So as we can see all these data points fall under the smooth curve, so we can calculate the tangent at different locations say we can write column 3. Here for each concentration we can calculate from here the $\frac{dC_A}{dt}$ that is the tangent. So for the first case it would be

$$\frac{10-0}{0-75} = -0.1333$$

Similarly, for this case it would be

$$\frac{10-0}{-3-94} = -0.1031$$

So on. So we can calculate all these data points and we will get for 1 it will be

$$\frac{3-1}{-10-300} = 0.0065$$

So the other data points we can write is -0.0658 then -0.0410, -0.0238 and -0.0108 and 0.0065.

So these are the $\frac{dC_A}{dt}$ values from this concentration versus time plot we can draw different tangents and we can calculate different $\frac{dC_A}{dt}$.

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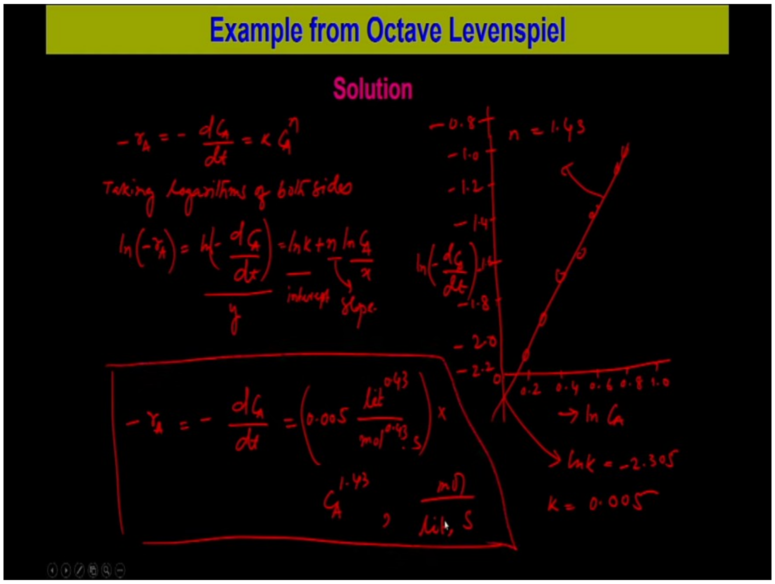

Example from Octave Levenspiel

Solution

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

Taking logarithms of both sides

$$\underbrace{\ln(-r_A) = \ln\left(-\frac{dC_A}{dt}\right)}_{y} = \underbrace{\ln k}_{\text{intercept}} + \underbrace{n}_{\text{slope}} \underbrace{\ln C_A}_{x}$$

$$\boxed{-r_A = -\frac{dC_A}{dt} = \left(0.005 \frac{lit^{0.43}}{mol^{0.43} \cdot s}\right) \times C_A^{1.43}, \quad \frac{mol}{lit \cdot s}}$$

So now we need to guess kinetics say nth order kinetics,

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

and we need to take log as we have taking logarithms of both sides so then we can write this is

$$\ln(-r_A) = \ln(-\frac{dC_A}{dt}) = \ln k + n \ln C_A$$

So as we have said this is y, this is intercept, this is slope and this is x. So this is, now if we plot the data, so this is zero and concentration is say 0.2, say 0.4, 0.6, 0.8, say 1.0, so this is $\ln C_A$ values. And the $\ln(-\frac{dC_A}{dt})$ as we have calculated earlier we can plot them.

So this is -2.2, so this is say 0.2, this is 1.8, this is 1.6, this is 2.0 and this is say 1.4, -1.4, this is -1.2, this is -1.0 and this is -0.8. So now, if we plot the data we can see that the data would be fitted like this. So it will give the intercept here is about ln k is about -2.305 and we would obtain k from here k = 0.005 and the slope from here we will get n = 1.43.

So if we use this data we can write the kinetic rate form which is

$$-r_A = -\frac{dC_A}{dt} = 0.005\frac{liter^{0.43}}{mole^{0.43}\sec ond}$$

This is $kC_A^{0.43}$ and the unit is $\frac{liter^{0.43}}{mole^{0.43}\sec ond}$. So this is how we can obtain the rate equation or the kinetic form of the particular reactions using the differential method of analysis.

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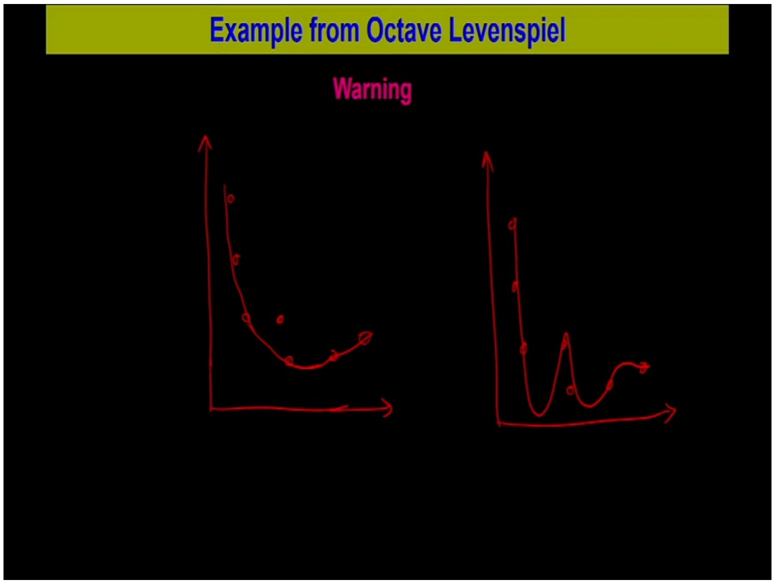

Example from Octave Levenspiel

Warning

Now one warning for this case, to use a differential form as we have said the data should be fitted with a guide with the eye that means if the data are like this and if we plot with a guide with the eye we would have drawn the data which would connect this with a smooth curve. But, if we the same data if we plot with a computer with polynomial fitting say our data is like this. So our data is like this and we want to fit a 5 degree or 6 degree polynomial, the polynomial may fit the data like this, like this. So it will take all the data points.

So this could lead to disasters for the analysis of the differential form of the rate equations, that is why for analysis of the differential form of the rate equations we must have the most accurate data which we can by which we can draw a smooth line and in general the kinetic data are sometimes scattered. So we need to draw the smooth line with a guide with our eyes instead of drawing with different degrees of polynomials in a computer program.

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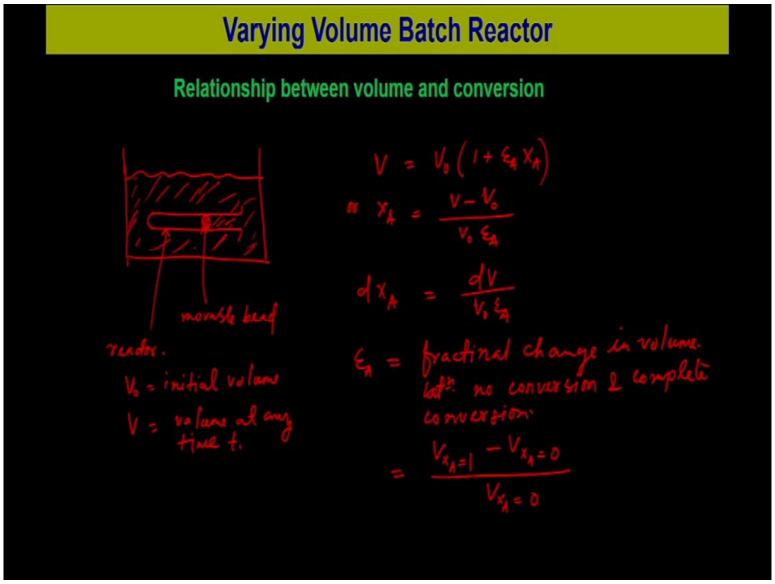

Varying Volume Batch Reactor

Relationship between volume and conversion

V_0 = initial volume

V = volume at any time t.

$$V = V_0(1+\varepsilon_A X_A)$$

or $$X_A = \frac{V - V_0}{V_0 \varepsilon_A}$$

$$dX_A = \frac{dV}{V_0 \varepsilon_A}$$

ε_A = fractional change in volume. betn. no conversion & complete conversion.

$$= \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

Now, let us consider varying volume batch reactors and how to analyze them by differential method as well as integral method of analysis. The varying volume reactors are most conveniently used in case of the micro processing field. Suppose, if we consider a very small reactor like this, so we can consider a bead kept over here in tube and then as soon as the reaction proceeds the bead will move from, so this is movable bead and this is the reactor. The initial volume is V_0 and V is the volume at any time t. So this is an example of variable volume systems and in general what we do we operate this reactor at constant pressure and isothermal conditions that means as soon as the reaction volume changes we move the bead keep the total pressure of the reactors same. In general we keep to operate this reactor isothermally.

So, if we consider volume and conversion relations is linear we can write for this case V at any time volume would be related to

$$V = V_0(1+\varepsilon_A X_A)$$

or from here we can write

$$X_A = \frac{V - V_0}{V_0 \varepsilon_A}$$

Now, if we differentiate this we can get

$$dX_A = \frac{dV}{V_0 \varepsilon_A}$$

So here ε_A is the fractional change in volume. So this fractional change of volume happens between no conversion and complete conversion between no conversion and complete conversion.

So as per the definition we can write

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

Complete conversion. So V_{X_A} is equals to 0 that is no conversion and V_{X_A} is equal to 1 complete conversion divided by V_{X_A} equals to 0. So this is by definition ε_A is the fractional change in volume between no conversion and complete conversion.

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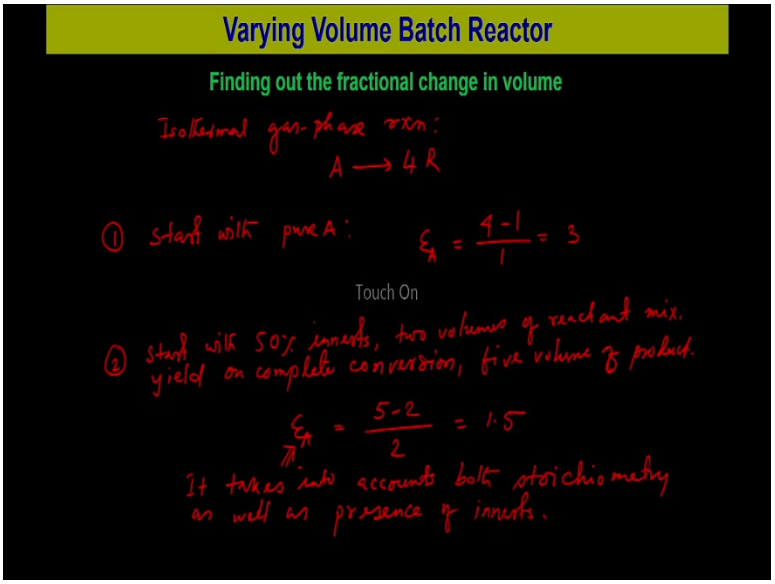

Varying Volume Batch Reactor

Finding out the fractional change in volume

Isothermal gas-phase rxn:

$A \longrightarrow 4R$

① Start with pure A: $\varepsilon_A = \frac{4-1}{1} = 3$

Touch On

② Start with 50% inerts, two volumes of reactant mix. yield on complete conversion, five volume of product.

$\varepsilon_A = \frac{5-2}{2} = 1.5$

It takes into accounts both stoichiometry as well as presence of inerts.

Now, let us take an a reactions and see how to calculate epsilon. So, now we will find out the fractional change in volume.

Say, consider an isothermal gas phase reaction

$$A \rightarrow 4R$$

Now, if we start the reactant A, start with pure A so then ε_A would be as per the stoichiometry 1 mole of A produce 4 mole of R. So it would be

$$\varepsilon_A = \frac{4-1}{1} = 3$$

So, ε_A would be 3. Now, in the second case if we start with 50% inerts with two volumes of reactant mixture yield on complete conversion 5 volume of product.

So that means if we take 2 volumes of A it will produce as per the stoichiometry 8 volumes of R but we had 50% inerts so we had 1 volume to 4 volume products. So total five volumes and we had 50% inerts with it. So,

$$\varepsilon_A = \frac{5-2}{2} = 1.5$$

So from here we can see that the epsilon it depends, or it takes into accounts both stoichiometry as well as the presence of inerts.

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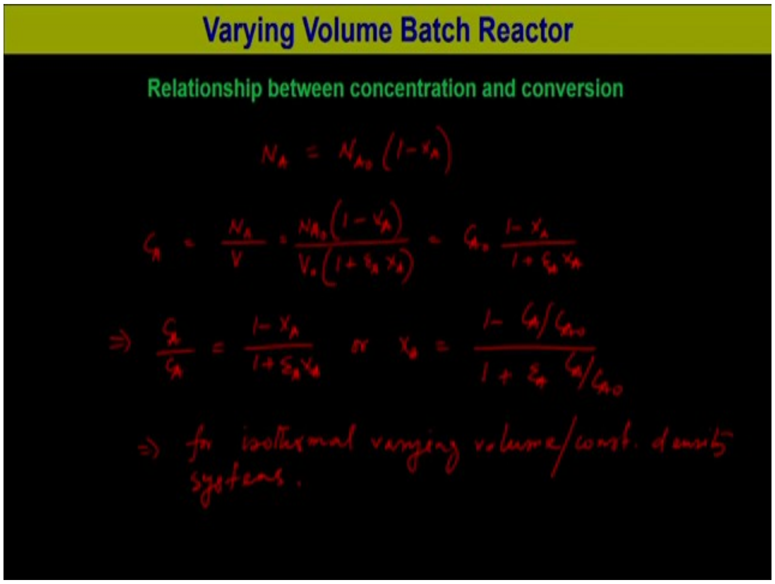

Varying Volume Batch Reactor

Relationship between concentration and conversion

$$N_A = N_{A0}(1-X_A)$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0(1+\varepsilon_A X_A)} = C_{A0}\frac{1-X_A}{1+\varepsilon_A X_A}$$

$$\Rightarrow \frac{C_A}{C_{A0}} = \frac{1-X_A}{1+\varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1-C_A/C_{A0}}{1+\varepsilon_A C_A/C_{A0}}$$

$\Rightarrow$ for isothermal varying volume/const. density systems.

So now, we will see the relations between the concentration and the conversion so concentration versus conversion relationship for varying volume batch reactor. So we know that N_A is the moles at any time would be related to

$$N_A = N_{A0}(1-X_A)$$

This is we have seen from the stoichiometry. Now, we can write

$$C_A = \frac{N_A}{V}$$

Now in this case this V is related with the fractional change in volume so we can write

$$= \frac{N_{A0}(1-X_A)}{V_0(1+\varepsilon_A X_A)}$$

So this we can write

$$= C_{A0}\frac{1-X_A}{1+\varepsilon_A X_A}$$

So if we just rearrange this we can write

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

or if we rearrange this it would be

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

So this is the relations between the concentration and conversion for isothermal varying volume or constant density system. This is for isothermal varying volume or constant density systems.

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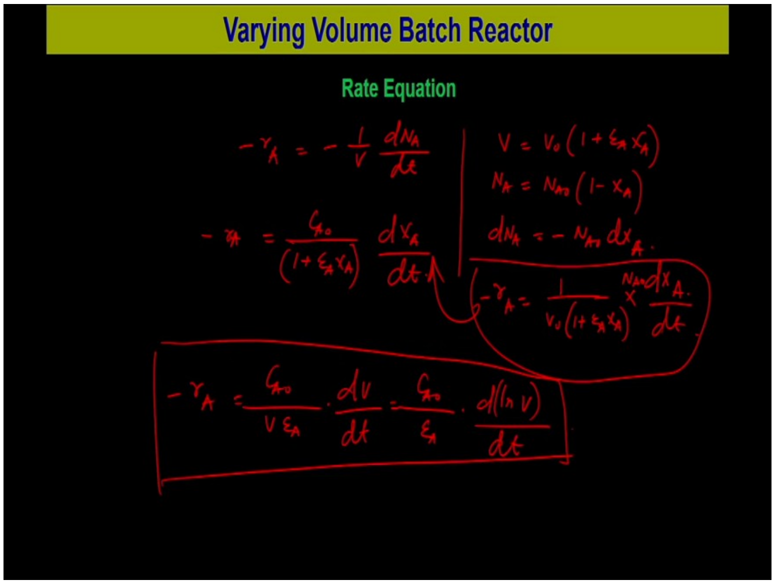

Varying Volume Batch Reactor

Rate Equation

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

$$-r_A = \frac{C_{A0}}{(1+\varepsilon_A X_A)}\frac{dX_A}{dt}$$

$$V = V_0(1+\varepsilon_A X_A)$$

$$N_A = N_{A0}(1-X_A)$$

$$dN_A = -N_{A0}\,dX_A.$$

$$-r_A = \frac{1}{V_0(1+\varepsilon_A X_A)} \times \frac{N_{A0}\,dX_A}{dt}.$$

$$\boxed{-r_A = \frac{C_{A0}}{V\varepsilon_A}\cdot\frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A}\cdot\frac{d(\ln V)}{dt}}$$

Now, the rate equations for varying volume batch reactors we can write

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

Now, if we substitute V and N_A so then this relations will come in terms of the conversion. So this would be

$$-r_A = -\frac{C_{A0}}{1+\varepsilon_A X_A}\frac{dX_A}{dt}$$

This can be obtained as we know

$$V = V_0(1+\varepsilon_A X_A)$$

and

$$N_A = N_{A0}(1-X_A)$$

So we can calculate

$$dN_A = -N_{A0}dX_A$$

So if we substitute these two over here then we will get

$$-r_A = \frac{1}{V_0}\frac{1}{1+\varepsilon_A X_A} N_{A0}\frac{dX_A}{dt}$$

So from here we can write this.

Now, in terms of the volume we can write this equation

$$-r_A = \frac{C_{A0}}{V\varepsilon_A}\frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt}$$

So this is in terms of the volume.

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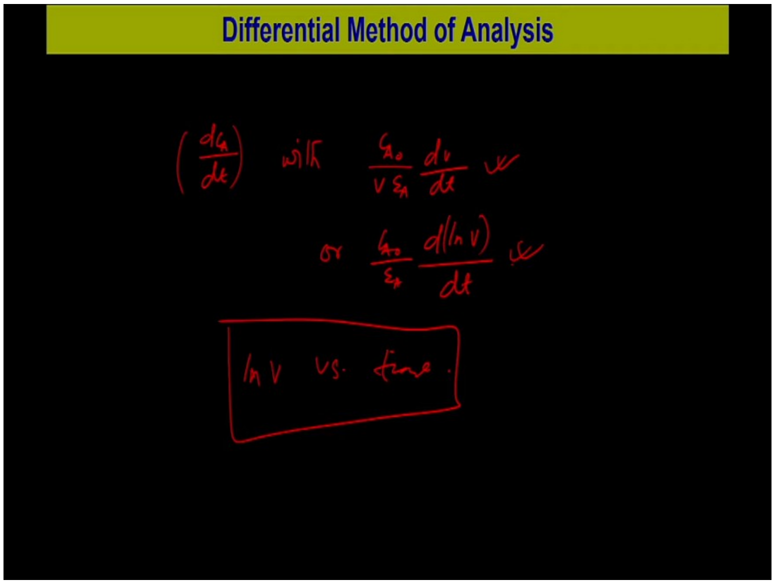

Differential Method of Analysis

$\left(\frac{dC_A}{dt}\right)$ with $\frac{C_{A0}}{V\varepsilon_A}\frac{dV}{dt}$ ✓

or $\frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt}$ ✓

$\boxed{\ln V \text{ vs. time.}}$

Now, if we consider differential method of analysis for the varying volume batch systems the procedure for the analysis for the varying volume batch reactor data using the differential method of analysis would be similar as we have done for the constant volume systems. In this case the $\frac{dC_A}{dt}$, this term would be replaced with either $\frac{C_{A0}}{V\varepsilon_A}\frac{dV}{dt}$ or $\frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt}$.

So all other method of analysis are same like

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

So in this case the $\frac{dC_A}{dt}$ for the varying volume systems we have to substitute with this term or with this term. So then the method of analysis that we have done just before it would be similar, so this means that we need to plot ln V versus time. And then calculate the slope.

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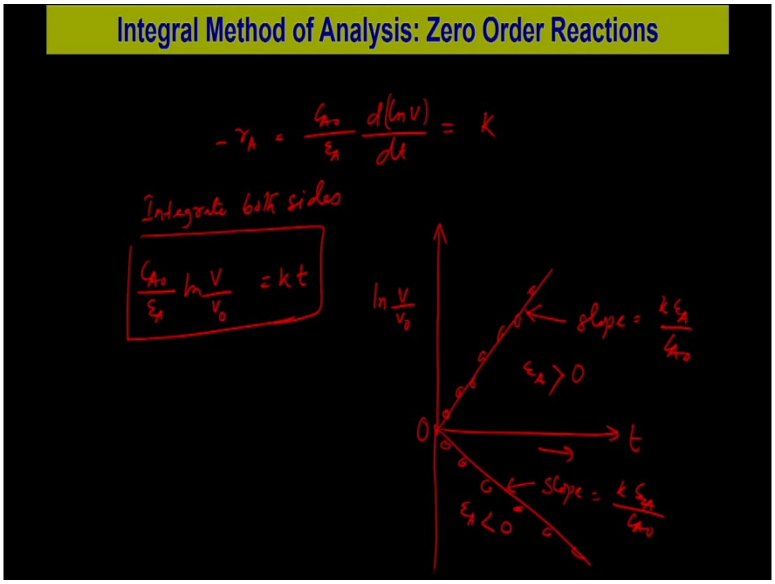

Integral Method of Analysis: Zero Order Reactions

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = k$$

Integrate both sides

$$\boxed{\frac{C_{A0}}{\varepsilon_A}\ln\frac{V}{V_0} = kt}$$

Now, let us consider the Integral method of analysis. First let us consider zero order homogeneous batch reactor data for first order system and since it is a for a zero order system since it is a zero order it is independent of the concentration so the rate equations would be

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = k$$

Now if we just integrate so we will have

$$\frac{C_{A0}}{\varepsilon_A}\ln\frac{V}{V_0} = kt$$

So this is the integral form of the zero order reactions.

Now, if we plot $\ln\frac{V}{V_0}$ versus time, so we would obtain a straight line passing through the origin with a slope is equal to $\frac{k\varepsilon_A}{C_{A0}}$. This is when $\varepsilon_A > 0$, when it is less than zero so the curve will lie in the opposite direction, so it would be like this and slope would be same; $\frac{k\varepsilon_A}{C_{A0}}$ and this is only for epsilon A < 0. So in this way we can test the zero order reactions by integral method of analysis for the varying volume systems.

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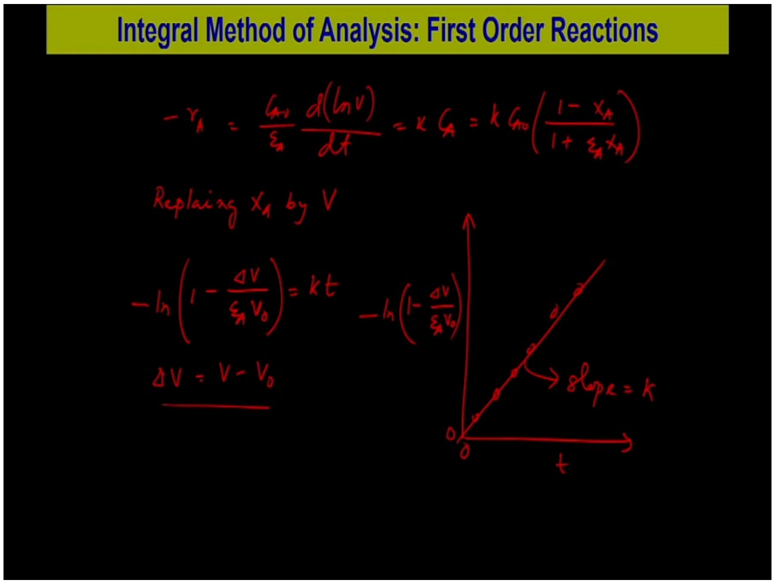

Integral Method of Analysis: First Order Reactions

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = k C_A = k C_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)$$

Replacing X_A by V

$$-\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right) = kt$$

$$\Delta V = V - V_0$$

Now, let us consider the first order reactions, so for first order reactions let us consider unimolecular type of reactions and as we have considered in case of the constant volume systems it would be similar, it would be

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A$$

This is first order, so we can write the C_A; we know the relationship C_A versus conversion. So

$$kC_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)$$

Now if we replace X_A by V and then integrate from the earlier equations which we have derived the relation between X_A and V, if we substitute that over here and then integrate so we would obtain

$$-\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right) = kt$$

So here $\Delta V = V - V_0$.

So now, if we plot $-\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right)$ versus time so the data would be fitted with a straight line passing through the origin and from the slope we would obtain values of k. So if it passes through origin with fitting with a straight line so then this follows the first order kinetics. So this way we can solve the say first order reactions for varying volume systems.

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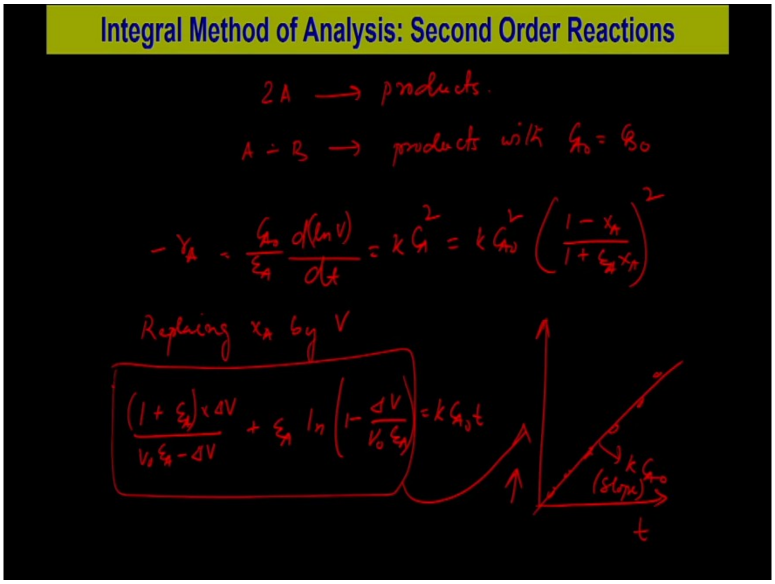

Integral Method of Analysis: Second Order Reactions

$2A \longrightarrow$ products.

$A + B \longrightarrow$ products with $C_{A0} = C_{B0}$

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A^2 = kC_{A0}^2\left(\frac{1-x_A}{1+\varepsilon_A x_A}\right)^2$$

Replacing x_A by V

$$\boxed{\frac{(1+\varepsilon_A)\times\Delta V}{V_0\varepsilon_A-\Delta V} + \varepsilon_A\ln\left(1-\frac{\Delta V}{V_0\varepsilon_A}\right) = kC_{A0}t}$$

Now, if we consider the second order reactions, let us consider bimolecular type of second order reactions say

$$2A \rightarrow products$$

Or we can consider

$$A + B \rightarrow products$$

With $C_{A0} = C_{B0}$. Then we can write

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A^2$$

Now, if we substitute this concentration terms like earlier it would be

$$= kC_{A0}^2\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^2$$

Now similar way like first order, replacing X_A by V relation we would obtain after the integration with algebraic manipulations we will get

$$\frac{(1+\varepsilon_A)\Delta V}{V_0\varepsilon_A - \Delta V} + \varepsilon_A \ln\left(1 - \frac{\Delta V}{V_0\varepsilon_A}\right) = kC_{A0}t$$

So now, if we plot either so this part versus time it would fit the data passing through the origin so it is a straight line passing through the origin with a slope, kC_{A0} is the slope. So this way we can solve the second order reactions by integral method of analysis from the varying volume batch reactor data.

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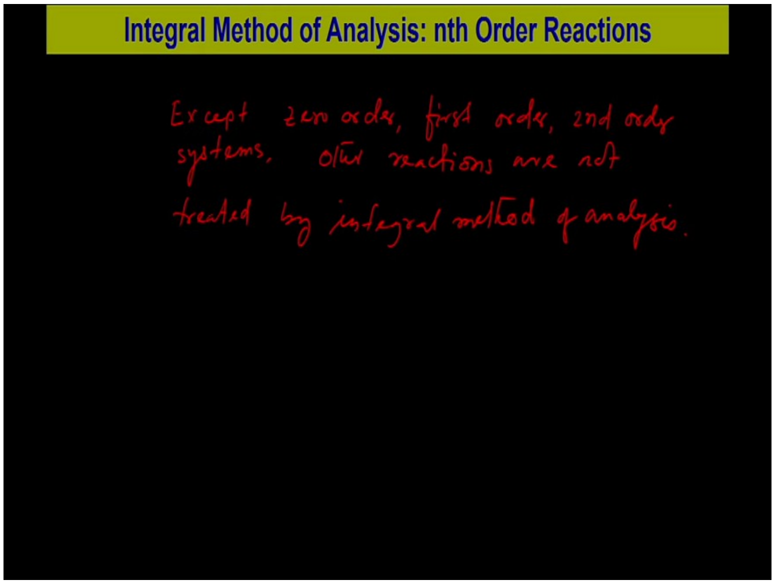

Integral Method of Analysis: nth Order Reactions

Except zero order, first order, 2nd order systems, other reactions are not treated by integral method of analysis.

So now if we take nth order reactions it is similar to the constant volume systems, we consider nth order kinetics and then fit the data by the integral method. As you can see it is not the straightforward as in the case of the constant volume systems. So in general except zero order, first order, second order systems, other reactions are not treated by integral method of analysis, since the higher order reactions are a bit complicated and in general it is not treated using this integral method of analysis.

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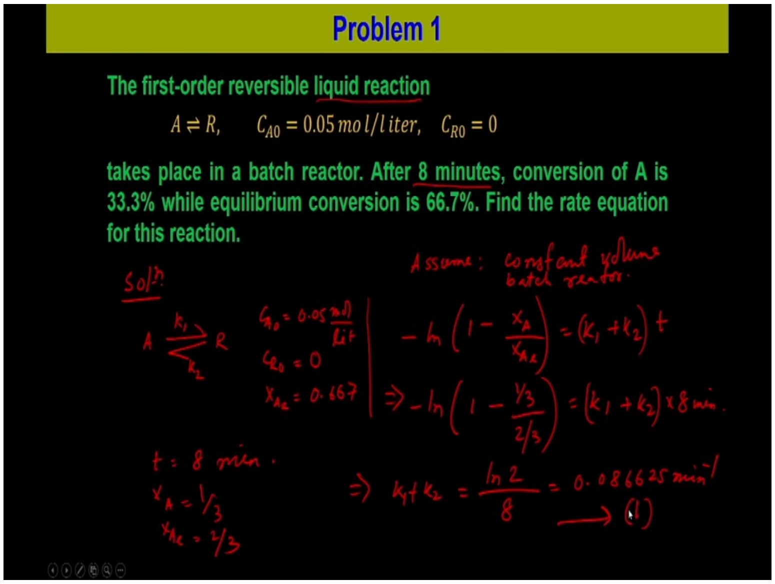

Problem 1

The first-order reversible liquid reaction

$A \rightleftharpoons R, \quad C_{A0} = 0.05\, mol/liter, \quad C_{R0} = 0$

takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction.

Assume: constant volume batch reactor.

Soln:

$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$

$C_{A0} = 0.05 \frac{mol}{lit}$

$C_{R0} = 0$

$X_{Ae} = 0.667$

$t = 8$ min.

$X_A = 1/3$

$X_{Ae} = 2/3$

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = (k_1 + k_2)t$$

$$\Rightarrow -\ln\left(1 - \frac{1/3}{2/3}\right) = (k_1 + k_2) \times 8 \text{ min.}$$

$$\Rightarrow k_1 + k_2 = \frac{\ln 2}{8} = 0.086625 \text{ min}^{-1} \longrightarrow (1)$$

Now, let us take some problem to see the how to use those methods which we have discussed for constant volume as well as the varying volume systems. Say first order reversible liquid phase reactions $A \rightleftharpoons R$ and concentrations C_{A0} is given 0.05 mole per liter, C_{R0} is equal to 0 and which is taking place in a batch reactor and after 8 minutes conversion of A is 33.3% while equilibrium conversion is 66.7%. We need to find the rate equation for this reaction.

So solution for this we can do, we have reversible reaction $A \rightleftharpoons R$, let us consider the forward reaction rate is k_1 and reverse reaction rate is k_2. It is given that C_{A0} is equal to 0.05 mole per liter and C_{R0} is equal to 0 that means no react product is present at the beginning, equilibrium conversion is given that is X_{Ae} is equal to 0.667 that is 66.7 percent conversion.

Now if we take A, assume the constant volume batch reactor that is our assumption. Now as it is happening in the liquid phase, so we can consider constant volume batch reactor and then the second order kinetics as we have derived earlier we can write the integral form of the equations

$$-\ln\left(1-\frac{X_A}{X_{Ae}}\right)=(k_1+k_2)t$$

Now, if we replace the values which are given from here, k_1 and k_2 from these relations we can obtain the relations between k_1 and k_2. So if we substitute the values

$$-\ln\left(1-\frac{1/3}{2/3}\right)=(k_1+k_2)8$$

So from here, we will get

$$k_1+k_2=\frac{\ln 2}{8}=0.086625\,\text{min}^{-1}$$

So this is a relation of k_1+k_2 say this is Equation 1.

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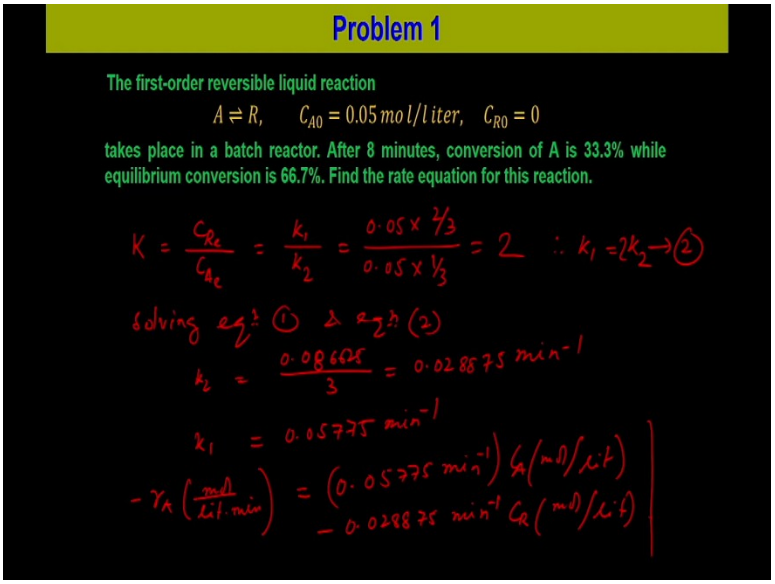

Problem 1

The first-order reversible liquid reaction

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takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction.

$$K = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{0.05 \times 2/3}{0.05 \times 1/3} = 2 \quad \therefore k_1 = 2k_2 \rightarrow ②$$

solving eqn ① & eqn (2)

$$k_2 = \frac{0.086625}{3} = 0.028875\ min^{-1}$$

$$k_1 = 0.05775\ min^{-1}$$

$$-r_A \left(\frac{mol}{lit.min}\right) = \left(0.05775\ min^{-1}\right) C_A (mol/lit) - 0.028875\ min^{-1}\, C_R (mol/lit)$$

Now from the thermodynamics we know that the equilibrium constant k is equal to C_{Re}, equilibrium concentration of the product divided by C_{Ae} equilibrium concentration of the reactant is equal to $\frac{k_1}{k_2}$. And this would be equal to,

$$K = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{0.05 * 2/3}{0.05 * 1/3} = 2$$

So therefore, $k_1 = 2k_2$, so this is equation 2.

So now, if we solve equation 1 and equation 2 we can get k_1 and k_2. So solving equation 1 and equation 2, we obtain

$$k_2 = \frac{0.086625}{3} = 0.028875\,\text{min}^{-1}$$

And

$$k_1 = 0.05775\,\text{min}^{-1}$$

So now, we can write the rate equation as

$$-r_A = \left(0.05775\,\text{min}^{-1}\right) C_A \left(mol/lit\right) + \left(0.028875\,\text{min}^{-1}\right) C_R \left(mol/lit\right)$$

So this is the rate expression of the reversible first order reactions $A \rightleftharpoons R$ and this way we can solve the problem of the batch reactor data.

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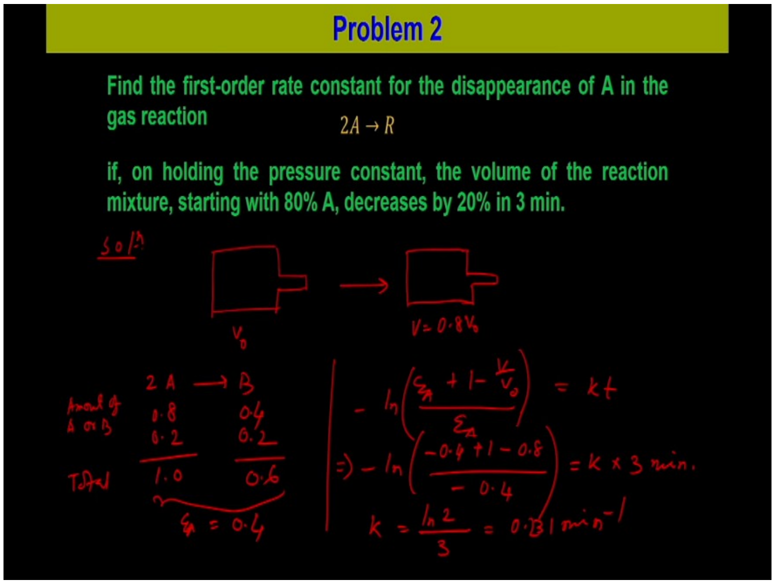

Problem 2

Find the first-order rate constant for the disappearance of A in the gas reaction

$$2A \rightarrow R$$

if, on holding the pressure constant, the volume of the reaction mixture, starting with 80% A, decreases by 20% in 3 min.

Sol^n

	$2A$	$\longrightarrow$	B
Amount of A or B	0.8		0.4
	0.2		0.2
Total	1.0		0.6

$\varepsilon_A = 0.4$

$$-\ln\left(\frac{\varepsilon_A + 1 - \frac{V}{V_0}}{\varepsilon_A}\right) = kt$$

$$\Rightarrow -\ln\left(\frac{-0.4 + 1 - 0.8}{-0.4}\right) = k \times 3 \text{ min.}$$

$$k = \frac{\ln 2}{3} = 0.231 \text{ min}^{-1}$$

Now, if we consider another problem of variable volume systems the first order rate constant for the disappearance of A in the gas phase reaction say $2A \rightarrow R$. And if on holding the pressure constant, the volume of the reaction mixture starting with 80 percent A decreases by 20 percent in 3 minutes.

So in this case we can solve say initial volume of the reactor, this is V_0 and then we can change the volume, this is $V = 0.8V_0$ and the reaction is $2A \rightarrow B$. Amount of A or B this is 0.8 and this is 0.4, from the stoichiometry inert initially 0.2 so it will remain 0.2. So total if we consider total, we will get this is 1 and this is 0.6. So from here ε_A is 0.4. Since this is first order reactions as we have derived for varying volume systems, we can write

$$-\ln\left(\frac{\varepsilon_A + 1 - \dfrac{V}{V_0}}{\varepsilon_A}\right) = kt$$

So if we substitute the values this would be

$$-\ln\left(\frac{-0.4 + 1 - 0.8}{-0.4}\right) = k * 3\,\text{min}$$

So from here we can calculate k

$$k = \frac{\ln 2}{3} = 0.231\,\text{min}^{-1}$$

So this way we can solve the varying volume batch reactor data using integral method of analysis for the first order systems. So this is overall we have covered, how to analyze the batch reactor data for constant volume and varying volume systems using both integral method of analysis and the differential method of analysis.

Now in the next lecture, we will start with another module which will cover the reactor design for the chemical reactions. Thank you very much for attending this lecture.