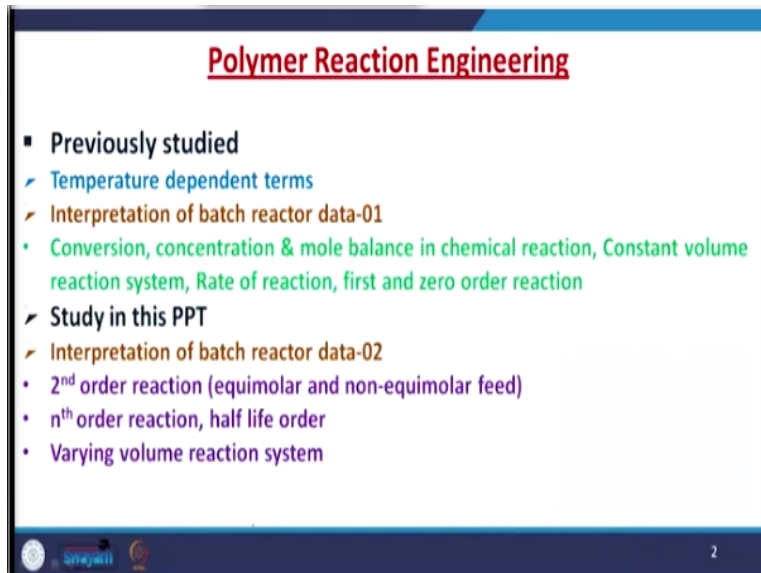


Polymer Reaction Engineering
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Lecture-16
Interpretation of Batch Reactor Data-III

Welcome to the next phase of interpretation of batch reactor data for reactor design. This is another segment of interpreting the batch reactor data which we obtained from various course of equations which we developed in previous lectures. So, let us have a brief look about that what we studied previously. We discussed about various temperature dependent terms; they are responsible for the various control activities in polymerization reactor.

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Polymer Reaction Engineering

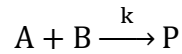
- Previously studied
 - Temperature dependent terms
 - Interpretation of batch reactor data-01
 - Conversion, concentration & mole balance in chemical reaction, Constant volume reaction system, Rate of reaction, first and zero order reaction
- Study in this PPT
 - Interpretation of batch reactor data-02
 - 2nd order reaction (equimolar and non-equimolar feed)
 - nth order reaction, half life order
 - Varying volume reaction system

2

Then we discussed about the conversion, concentration, mole balance, in various chemical reactions under the head of interpretation of batch reactor data. We had a discussion about the constant volume reaction system, then we started the rate of reaction and achieved up to the first and zero order reaction. Now in this particular lecture we are going to study about the interpretation of batch reactor data phase 2.

Now this comprises various second order reactors or reactions both equimolar and non-equimolar feed. Then we will discuss about the nth order reaction along with the half-life concept of reaction scheme. Then we will discuss about the varying volume reaction system, so let us start with the

second order reaction scheme. Now this is a bit mathematical one, now suppose a second order bimolecular irreversible reaction is occurring with the reactants say A and B and they produced the product P.



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Interpretation of batch reactor data

➤ 2nd order reaction (n=2)

Suppose a second-order bimolecular irreversible reaction occurring with reactant A and B and produced product P which is represented as:

$$A + B \xrightarrow{k} P$$

The rate equation for the above chemical reaction can be written as:

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

So, let us have a broad mathematical representation of this particular reaction like A + B, here our known reaction constant and it is the P, P stands for the product. So, the rate equation for this particular chemical reaction it can be written as for $-r_A$, if you recall that in the previous lecture we said that A and B both are consuming in the reaction mass. So, we use to denote their rate as minus because they are consuming and whatever product you are getting that is being accumulated.

And that is being generated into your course of time that is it is represented as with plus sign. So, this is equal to $-dC_A$, recall C represents the concentration, so C_A represents the concentration of A over the period of time. And this is represented as kC_A , sorry this is beta, right, now these are the stoichiometric coefficients.

The rate equation for the above chemical reaction can be written as:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A^\alpha C_B^\beta$$

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Interpretation of batch reactor data

➤ 2nd order reaction ($n=2$) $\rightarrow A + B \rightarrow C + D$

As, for elementary chemical reaction, the order of the reaction is the sum of the stoichiometric coefficient raise to the power of concentration terms in the rate law i.e.

The overall order of reaction (n)
 $n = \alpha + \beta$
 $n = 1 + 1 = 2$
 $=$

$A + B \xrightarrow{k_i} P$

Now as for the elementary chemical reactions, in question the order of reaction is usually the sum of stoichiometric coefficient raised to the power of a concentration term in the rate law. Now see before we go into the detail let us have a look about the stoichiometric coefficient or stoichiometric number. If you recall previously, we studied about the reaction like $aA + b$. Now here these are the reactants and these are the product profiles and associated numbers they are referred as either stoichiometric number or stoichiometric coefficient.

So as far as again go back to the elementary chemical reaction now; if we try to represent this thing mathematically, the overall order of reaction say n , now n if you recall the previous one, here we mentioned alpha and beta these are the stoichiometric coefficients of this particular reaction, so $n = \alpha + \beta$. Now if we take the second order the thing into cognizance, then n will be 2.

$$n = \alpha + \beta$$

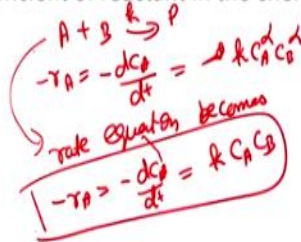
$$\Rightarrow n = 1 + 1 = 2$$

Now from where this one and one they came into existence, if you recall that we discussed this equation $A + B = P$. Now here the coefficient number of stoichiometric coefficient of A is 1 and stoichiometric coefficient of B is 1, so that is why the order of reaction is 2.

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Interpretation of batch reactor data

And in the chemical reaction, the value of corresponding order with respect to the reactant A and B in the rate law is equal to one, hence the overall order of the reaction is two, which is same as sum of the stoichiometric coefficient of reactant in the chemical reaction.



Now and if we say that the chemical reaction in any kind of a chemical reaction the value of corresponding order with respect to the reactant A and B in rate law is equal to 1, hence the overall order of reaction is usually 2. So, usually when we talk about which is same as the sum of the stoichiometric coefficient of reaction in chemical reaction. So, usually when we talk about any kind of chemical reaction, so you need to put this stoichiometric coefficient into the consideration and they play a very vital role in this type of aspect.

So, if you see that if you recall the previous equation which was the rate equation for this particular reaction, you see that we have given this $r_A = -dC_A$ upon dt . Now for this the rate equation becomes $-r_A$, so this is my rate equation. So, this thing is the very important for interpreting the batch reactor data while we go for further reactor design in any kind of chemical reaction or any kind of polymerization reaction.

Now for equimolar concentration of a reactant A, let us say that both reactants A and B are having the property of equimolar. So, or in other words we say that when the concentration of reactant A and B are equal in amount.

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Interpretation of batch reactor data

▪ For equimolar concentration of reactants A and B

When the concentration of the reactants A and B are equal in amount to be feed i.e. $C_{A0} = C_{B0}$, then from the above rate equation we can write it as.

$C_{A0} = C_{B0}$
 $C_A = C_B$
 $C_{A0} \text{ \& } C_{B0} \rightarrow t=0$
the rate equation in this case
be comes
 $-r_A = -\frac{dC_A}{dt} = kC_A^2$

So, that we can see that $C_{A0} = C_{B0}$, now here C_{A0} and C_{B0} these are the concentration at time $t = 0$, concentration of both A and B at time $t = 0$. So, starting concentration you can see that this is same C_{A0} and C_{B0} . So, if we are saying that we are having the equimolar concentration, so in that case $C_{A0} = C_{B0}$. Or in other words we can say $C_A = C_B$ for. So, the rate equation in this case becomes $-r_A = -\frac{dC_A}{dt}$, this is original equation, now this is equal to.

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

So, this is your rate equation for equimolar concentration of reactant A and B and this is the very common practice across in polymerization reaction engineering or chemical reaction engineering. Now again go back to this particular thing that if we try to rearrange and integrate with the initial conditions, that is the concentration may vary from say C_{A0} to C_A from time $t = 0$ to t .

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \int_0^t k dt$$
$$\Rightarrow \left[\frac{1}{C_A} - \frac{1}{C_{A0}} \right] = kt$$

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Interpretation of batch reactor data

▪ For equimolar concentration of reactants A and B $A+B \xrightarrow{k} P$

On rearranging and integrating with initial conditions: the concentration vary from C_{A0} to C_A and time $t = 0$ to t we have C_{A0} C_A

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

$$\Rightarrow kt = \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right)$$

Now this is a very common thing, now say if $A + B$ again gives you P , so over the period of time this A is getting depleted or it is being consumed in the course of a reaction mass. And say after t this initial concentration of C_{A0} becomes the concentration of C_A . So, in this case if we try to rearrange and integrate this initial condition then my equation will become this is your starting C_{A0} to C_A over the period of time t , this is the time t , this will become $dC_A k dt$.

So, if I wish to find out the rate constant, then we can utilize this particular equation or in other words you can say this equation will become. Now this is my final equation for representing this thing. So, by this way we are discussing the various integrities of batch reactor data sometimes you may have equimolar concentration of the reactant sometimes you may not. So, we must acquaint all kind of a scenario for achieving the better result to for prediction of any kind of reaction engineering data.

So, that is why we are discussing everything pertaining to this particular approach. Now for rate equation if sometimes people may ask that gentlemen this thing is very good. But sometimes we need to represent the rate equation in terms of conversion.

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Interpretation of batch reactor data

For rate equation in term of conversion, on putting the value of C_A in terms of conversion in the above equation, we have:

Concentration of reactant A after conversion X_A
at time 't'.

$$C_A = C_{A_0}(1 - X_A) = \frac{1}{1 + X_A} - 1 = C_{A_0}kt$$

$$\frac{1}{C_{A_0}(1 - X_A)} - \frac{1}{C_{A_0}} = kt$$

$$\left[\frac{X_A}{1 - X_A} \right] = C_{A_0}kt$$

$$\left[\frac{C_{A_0}kt}{1 - C_{A_0}kt} \right] = X_A$$

So, on putting the value of C_A in terms of the conversion in the previous equation which we developed over here. Then we may have the concentration of reactant A say after conversion X_A , X_A is the number of moles of component A or the reactant A. Now say after time t, at time t, so it is this $C_A = C_{A_0}$ if you recall that this is my initial concentration and this is X_A , now this may become $1 - X_A$.

In term of conversion, putting the value of C_A from equation in the equation we have

$$\Rightarrow \left[\frac{1}{C_{A_0}(1 - X_A)} - \frac{1}{C_{A_0}} \right] = kt$$

$$\Rightarrow \left[\frac{1}{(1 - X_A)} - 1 \right] = C_{A_0}kt$$

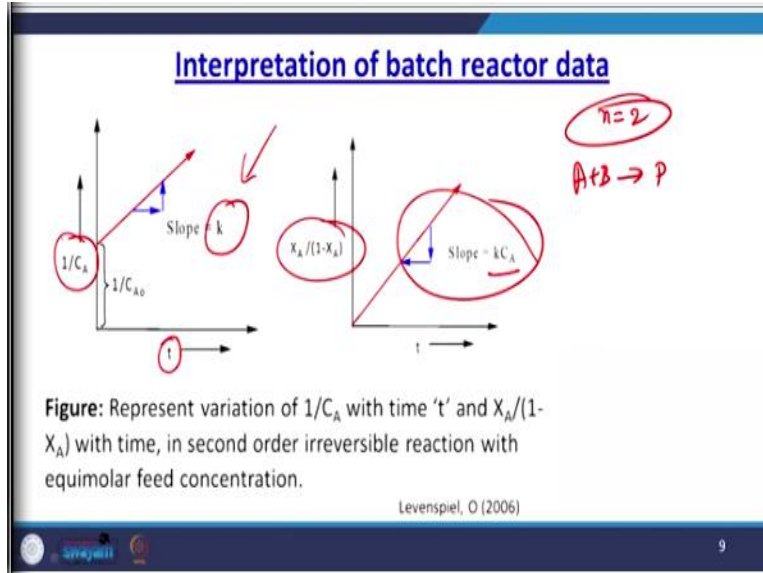
$$\Rightarrow \left[\frac{X_A}{(1 - X_A)} \right] = C_{A_0}kt$$

$$\Rightarrow \left[\frac{C_{A_0}kt}{(1 - C_{A_0}kt)} \right] = X_A$$

Now the genesis of this equation is 1 upon $C_{A_0}(1 - X_A)kt$. So, if we rearrange the things this may become X_A upon $(1 - X_A)$ or $C_{A_0}kt$ upon $1 - C_{A_0}kt$ this is X_A . So, by this way you can find out the conversion of the reactant A in different approaches. And sometimes this particular information is

extremely useful for prediction of any kind of data which is required for the designing of reactor or designing of other parameters for polymerization reaction. Now if sometimes it is a very useful practice to plot all these things and this is you can see the schematic diagram for the representation of variation of 1 upon C_A with time in this graph.

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And X_A upon $1 - X_A$ that is the mole fraction or conversion of component A or reactant A with the time, in this second order irreversible reaction were equimolar feed concentration. So, if you recall that we had this $n = 2$ that is the order of a reaction and both reactants $A + B$ are equimolar in nature. So, you see that this slope is represented by kC_A and similarly over here the slope is k if we try to plot with respect to time and inverse of concentration of A. So, these representation is very useful for prediction of any kind of unknown or prediction of any kind of the behavior of the batch reactor in due course of time.

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Interpretation of batch reactor data

Note :

- For second-order irreversible reaction, we cannot achieve the full conversion of reactant, as X_A is always less one (see the equation).
- Rate of change of X_A with respect to the time is a function of the initial concentration of the reactant. So, on the increase in the initial concentration of reactant, there is an increase in the conversion.

Now for second order irreversible reaction we cannot achieve the full conversion of reactants. As usually the X_A is always less than 1, if you see these previous equations, so you see that X_A is always less than 1. Now the rate of change of X_A with respect to the time is a function of initial concentration of a reactant. So, upon increasing the initial concentration of reactant, there is an increase in the conversion. So, that is a very important point for taking care of any kind of reaction engineering approaches. Now sometimes we may encounter another type of thing that is the bimolecular and irreversible second order reaction with non-equivalent molar feed of reactant A and B.

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Interpretation of batch reactor data

- Bimolecular & irreversible Second-order reaction with the non-equivalent molar feed of reactant A and B

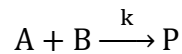


Suppose a bimolecular irreversible second-order reaction with different initial reactant concentration of A and B is consumed to form product P.

The expression for the reactant concentration A & B in terms of conversion after time 't' can be written as:

Now previously we discussed about the equimolar feed aspect where both A and B they were having the equimolar concentration. Now sometimes you may have a non-equimolar type of thing, maybe the concentration of this or number of moles of molar concentration of A maybe different with the molar concentration of B. So, let us try to solve this particular thing mathematically.

So, suppose a bimolecular irreversible second order reaction with the different initial reactant concentration of say A and B is consumed to form the product A, like this, this particular equation deals with this type of scenario.



Now expression for the reactant concentration A and B in terms of the conversion at time t may be given as.

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Concentration after time t with conv. conversion
 $C_A = C_{A0}(1 - X_A)$
 For reactant B
 $C_B = C_{B0} - C_{A0}X_A$
 Conversion of reactant A after time t (if reactant A is limiting)

So, the reactant concentration and after time t with respect to conversion is C_A is equal to $C_{A0}(1 - X_A)$.

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

Now for because here we are not considering the equimolar concept, so again we need to put the things related to the reactant B. So, for reactant B, we need to write C_B is equal to C_{B0} minus $C_{A0}X_A$, this is the conversion of reactant A after time t.

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

Now one condition is extremely essential in this approach, that it is applicable if the reactant A is limiting. So, this thing needs to be taken care while we calculate this type of situation. Now if we talk about the other rate expression for this particular reaction.

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Interpretation of batch reactor data

Rate expression for the reaction is;

Put the values of concentration of reactant A and B after time 't', and $-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = C_A \frac{dX_A}{dt}$ in the above equation then we have

$$-\frac{dC_A}{dt} = -C_{A0} \frac{dX_A}{dt} = k C_{A0} (1-X_A) (C_{B0} - C_{A0} X_A)$$

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The rate expression for the Chemical reaction

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

Now sometimes again this type of approach can be written as the rate for the chemical reaction is $-r_A dt C_A C_B$. Now 2 things are very important to at this juncture, one is that if you see that here $-r_A$ and this is because we are saying that A is the limiting reactant, so this is the governing factor, so $-dC_A$ upon $dt = -dC_B$ because the concentration of B is usually tutored by this particular approach and this is equal to kC_B .

So, on putting if we go to the things that if we put the values of concentration of a reactant A and B after time t. So, $dC_A dt$ or that $-dC_B$ upon $dt = C_A$ that is into $dX_A dt$ in this equation which we discussed earlier. So, it can be represented as $-dC_A dt$ which is equal to $kC_1 - X_A C_{B0}$, this is the initial concentration of reactant B. So, this is I can say the final outcome for this particular approach.

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Interpretation of batch reactor data

Let $M = C_{B0}/C_{A0}$ and put in the above expression and arranged, we have:

$$\frac{dX_A}{(1-X_A)\left(\frac{C_{B0}}{C_{A0}} - X_A\right)} = k C_{A0} dt$$

or

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

Now let us see sometimes it is very convenient to represent this particular approach, let us see that $m = C_{B0}$ upon C_{A0} . And if we put this thing into this previous expression and try to rearrange the things, then we may have this dX_A upon $1 - X_A$ which is equal to $k C_{A0} dt$. Or if we try to rearrange the things then it will become dX_A upon $1 - X_A$ into $M - X_A k C_{A0} dt$. So, this is my equation which we need to remember while interpreting such kind of thing in due course of time. Now next is that if we integrate the things this particular equation with the help of say initial conversion.

Rate expression for the reaction is;

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

Put the values of concentration of reactant A and B after time 't', and $-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = C_{A0} \frac{dX_A}{dt}$ in the above equation then we have

$$\Rightarrow -C_{A_0} \frac{dX_A}{dt} = kC_{A_0}(1-X_A)(C_{B_0} - C_{A_0}X_A)$$

Let $M = C_{B_0}/C_{A_0}$ and put in the above expression and arranged we have

$$\Rightarrow \frac{dX_A}{(1-X_A)\left(\frac{C_{B_0}}{C_{A_0}} - X_A\right)} = kC_{A_0} dt$$

On integrating the above equation with initial conversion $X_A=0$ to final conversion X_A at time 't' we have

$$\Rightarrow \int_0^{X_A} \frac{dX_A}{(1-X_A)(M - X_A)} = \int_0^t kC_{A_0} dt$$

On breakdown the above expression with partial fraction method we have found

$$\begin{aligned} \Rightarrow \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-1)} + \int_0^{X_A} \frac{dX_A}{(1-M)(M-X_A)} &= \int_0^t kC_{A_0} dt \\ \Rightarrow \frac{1}{(M-1)} \left[\int_0^{X_A} \frac{dX_A}{(1-X_A)} - \int_0^{X_A} \frac{dX_A}{(M-X_A)} \right] &= \int_0^t kC_{A_0} dt \\ \Rightarrow \left[\frac{1}{(M-1)} (-\ln(1-X_A)) \right]_0^{X_A} + \left[\frac{1}{(M-1)} \ln(M-X_A) \right]_0^{X_A} &= kC_{A_0} t \\ \Rightarrow \frac{1}{(M-1)} [-\ln(1-X_A) + \ln(M-X_A) - \ln(M)] &= kC_{A_0} t \\ \Rightarrow \frac{1}{(M-1)} \ln \left[\frac{(M-X_A)}{M(1-X_A)} \right] &= kC_{A_0} t \end{aligned}$$

or

$$\Rightarrow \ln \left[\frac{(M-X_A)}{M(1-X_A)} \right] = \ln \frac{C_B}{MC_A} = (M-1)kC_{A_0} t$$

This is required final result for calculation of conversion X_A after time 't' in second-order irreversible bimolecular reaction with non-equivalent reactant concentration. It is valid for all ratio of M but not for $M=1$.

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Interpretation of batch reactor data

On integrating the above equation with initial conversion $X_A=0$ to final conversion X_A at time 't' we have

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

On break down the equation with partial fraction method

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

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

Now initially there was no conversion at time $t = 0$, so $X_A = 0$ and if we achieve the final conversion X_A at time t then we can integrate the things in this particular approach. So, we may have the equation mathematical equation like this dX_A upon $1 - X_A M - X$ which is equal to 0 to $tkC_{A0} dt$. Now this is our previous equation, now on breakdown the above this equation our expression with the partial fraction. We have dX_A upon $1 - X_A + 0$ to $X_A dX_A$ upon $1 - M$ into $M - X_A$ which is equal to 0 to $tkC_{A0} dt$. Now this may become 1 upon $M - 1$ to $X_A dX_A$ upon $1 - X_A - 0$ to $X_A dX_A$ upon $M - X_A$, now these mathematical this is equal to 0 to $t k C_{A0} dt$.

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$$= \frac{1}{(M-1)} \left[-\ln(1-x_A) + \ln(M-x_A) - \ln(M) \right] = k C_{A0} t$$

$$\Rightarrow \int \frac{1}{M-1} \ln \left[\frac{M-x_A}{1-x_A} \right] = k C_{A0} t$$

$$\ln \left[\frac{M-x_A}{1-x_A} \right] = \ln \left[\frac{C_A}{C_{A0}} \right] = (M-1) k C_{A0} t$$

Now again if we keep on rearranging the things with respect to the mathematical approach this will become $-\ln(1 - X_A) + \ln(m - X_A) - \ln M$, this is equal to $kC_{A0}t$. So, again upon rearranging $M - 1 \ln$ this is equal to $kC_{A0}t$. So, this is my master equation or sometimes it can be represented as $\ln - M - 1$. Now this is again the rearranged form of this particular equation. So, this thing is again very important thing pertaining to the approaches associated with this type of prediction.

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Interpretation of batch reactor data

- ✓ This is required final result for calculation of conversion X_A after time 't' in second-order irreversible bimolecular reaction with non-equivalent reactant concentration.
- ✓ It is valid for all ratio of M but not for M=1.

Studyall 15

Now this particular thing is required the final result for the calculation of conversion X is say after time t in the second order irreversible bimolecular reaction with non-equivalent reactant conversion. Now you see there are so many conditions are embedded in this particular statement you are having nonequivalent you are having irreversible, you are having the bimolecular reactions, you are having the second order reaction.

So, usually it is this particular equation is valid for all ratio of M but not for M is = 1. So, this thing need to be remember while calculating such kind of approaches and performing the calculation for any kind of interpretation of batch reactor data. Now let us move to the n^{th} order reaction.

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Interpretation of batch reactor data

▪ For nth order reaction

The rate equation for nth order reaction is written as:

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

On rearranging and integrating the above equation with initial concentration C_{A0} at time $t=0$ to the concentration C_A at time 't' ($n \neq 1$) then we have found;

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

$t \rightarrow 0$
 $t \rightarrow t$

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Now the rate of this particular rate equation for this particular n^{th} order reaction can be represented like this - $r_A = kC_A^n$, this is the order, right.

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

Now on rearranging and integrating this particular equation with the initial concentration of C_{A0} at the time $t = 0$ to the concentration C_A at the time $t = t$ and where we know that n is not equal to 1. Then we can find that 1 upon $C_A^{n-1} - 1$ upon C_{A0}^{n-1} and $-1 = kt(n-1)$. Now this is the generalized equation where we are moving from time $t = 0$ to time $t = t$.

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

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Interpretation of batch reactor data

Note:

- If $n > 1$, then the reaction never go to complete in finite time
- If $n < 1$, then the reactant concentration will fall to zero and then becomes negative at a finite time interval.

But the real concentration of the reactant could not become negative, so the real limit for integration method is as given below, beyond which it is not applicable for real system.

$$C_A = 0 \text{ @ } t \geq \frac{C_A^{n-1}}{(1-n)k}$$

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Now if in this particular equation if you see that if n is greater than 1, then reaction never go to on completion infinite time. Now if n is less than 1 then the reactant concentration will fall to 0 and then becomes negative at the finite time of interval. Remember these there are only 3 possibilities in such kind of a scenario, one is that either n is less than 1 or n is greater than 1 or n is equal to 1. But we have eliminated this n is equal to 1, that is n is not equal to 1, so that is why we considered these 2 situation.

Now for as far as the real concentration of the reactant they could not become negative. So, the real limit of integration method is usually we are going to discuss in this particular approach beyond which it is not applicable for any kind of real system. So, this is the real scenario C_{A0} at $t = \frac{C_{A0}^{n-1}}{(1-n)k}$, so this is the scenario where you are having you can apply for the real system.

$$C_A = 0 \text{ at } t \geq \frac{C_A^{n-1}}{(1-n)k}$$

(Refer Slide Time: 28:19)

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Up to this stage we discussed about the second order reaction, we developed the methodology for or mathematical representation for batch reactor data interpretation for n^{th} order reaction. Subsequently in the next lecture we will discuss about the half-life because it is again a very integral part of your interpretation pattern of batch reactor. So, we will discuss about the half-life and other associated things, thank you very much.