

Polymer Reaction Engineering
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Lecture – 15
Interpretation of Batch Reactor Data - II

Welcome to the second segment of temperature dependent interpretation of batch reactor data. So, we were discussing about the interpretation of various batch reactor data in the previous lecture and we will continue this particular approach in this segment too. So, as you recall that previously we discussed the various parameters, various factors involved in the interpretation of batch reactor.

And how we can interpret those data with respect to the rate constant, with respect to the rate of reaction, with respect to the conversion, etc. We will continue this particular approach in this particular lecture too. So, let us have a look about the continuation of a rate of a reaction.

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Rate of reaction for constant volume system
 $-r_A = \frac{1}{V} \frac{dN_A}{dt}$
 $N_A = C_A V$
 $dN_A = d(C_A V)$
from rate equation
 $-r_A = \frac{1}{V} \frac{d(C_A V)}{dt}$

Now, rate of reaction if you recall the previous rate that can be written as rate of reaction for constant volume system. This is $\frac{1}{V} \frac{dN_A}{dt}$. Now, here N_A is $C_A V$ as you know that this is the volume. Now if we differentiate this equation, then this equation will become $dN_A = dC_A V$. Now from the rate equation, it can be represented as $-r_A = \frac{1}{V} \frac{dC_A V}{dt}$.

Rate of reaction:

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

Now from relation;

$$N_A = C_A V$$

$$-r_A = \frac{1}{V} \frac{d(C_A V)}{dt}$$

So, this is one of the equations to predict the rate of reaction. Now if we differentiate this equation with respect to other aspects, then that things may become more and more complicated.

On differentiate the above equation with respect to time 't'

$$-r_A = \frac{1}{V} \left(\frac{V d(C_A)}{dt} + \frac{C_A d(V)}{dt} \right)$$

But, for constant volume system $dV/dt = 0$.


$$\begin{aligned} -r_A &= \frac{1}{V} \left(\frac{V d(C_A)}{dt} \right) \\ \Rightarrow -r_A &= \left(\frac{d(C_A)}{dt} \right) \end{aligned}$$

It is Valid only for the constant volume reaction system.

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Interpretation of batch reactor data

On differentiate the above equation with respect to time 't', we have:

$$\begin{aligned} -r_A &= \frac{1}{V} \left(V \frac{dC_A}{dt} + C_A \frac{dV}{dt} \right) \\ \frac{dV}{dt} &= 0 \\ \Rightarrow -r_A &= \frac{1}{V} \left(V \frac{dC_A}{dt} \right) \quad (\text{Valid for Constant Volume System}) \\ -r_A &= \frac{dC_A}{dt} \\ -r_A &= C_{A0} \frac{dx_A}{dt} \quad \text{as } C_A = C_{A0}(1-x_A) \\ dC_A &= -C_{A0} \frac{dx_A}{dt} \end{aligned}$$


So, then in that case we can write this equation 1 upon V $V dC_A dt + C_A dV$. Now as we assume that this is a constant volume system, so in that case dV upon dt will become to 0 and then this equation will be represented as $-r_A = 1$ upon V $V dC_A dT$ and this is A upon dT . Now this is valid for constant volume system.

Now if we talk about with respect to the conversion, then it can be represented as $-r_A = C_{A0} \frac{dX_A}{dt}$ upon dT as $C_A = C_{A0}(1 - X_A)$ and $dC_A = -C_{A0} dX_A/dt$. So, we can utilize this particular thing to give you that desired result.

The rate in term of conversion can be written as

$$-r_A = -\frac{dC_{A0}(1 - X_A)}{dt}$$

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

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Interpretation of batch reactor data

❖ The kinetic equation for irreversible unimolecular different order reaction:

➤ For first order reaction

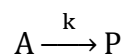
Suppose a first order reaction with reactant A is get converted into product P. The rate constant is k and initial concentration of reactant is C_{A0} , and concentration of reactant after time 't' is C_A .

$A \xrightarrow{k} P$

The rate equation can be written as:

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

Now, let us have a look about the kinetic equation for irreversible unimolecular different order reaction. So, as you know that there are various types of orders of the reaction. So, let us have a look about the first order reaction. Now, suppose the first order reaction with the reactant A is get converted into the product P.



As per this equation A is converted to P. The rate constant k and the initial concentration of reactant A is C_{A0} .

The rate equation can be written as

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

And the concentration of the reactants after time t is represented at C_A . So, the chemical first order reaction can be represented as $-r_A = -dC_A$ upon $dt = kC_A$. So, this is the first order reaction.

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Interpretation of batch reactor data

On rearrange and integrate the above equation with initial concentration C_{A0} at time $t=0$, and concentration C_A at time 't' we have get:

$$\begin{aligned} - \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} &= \int_0^t k dt \\ &= \ln \left(\frac{C_{A0}}{C_A} \right) = kt \\ \boxed{C_A = C_{A0} e^{-kt}} \end{aligned}$$

Required kinetic equation for first order reaction

Now on rearranging and integrating this equation with initial concentration C_{A0} at the time $t = 0$ and the concentration C_A at time t , we can get this equation like this integration from C_{A0} that is the initial concentration of reactant A to C_A dC_A upon $C_A = 0$ to t $k dt$. Now, here that $\ln C_{A0}$ upon C_A upon simplification it becomes like this or $C_A = C_{A0} e$ to the power $-kt$.

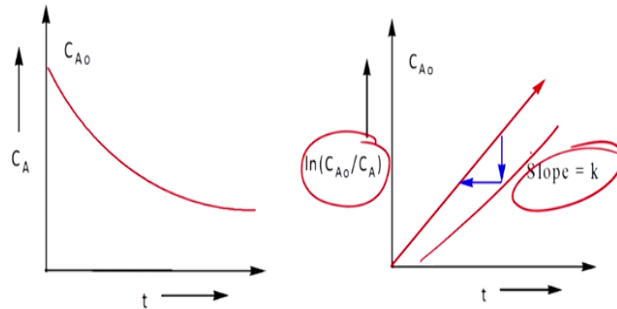
On rearrange and integrate the above equation with initial concentration C_{A0} at time $t=0$, and concentration C_A at time 't'.

$$\begin{aligned} - \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} &= \int_0^t k dt \\ \Rightarrow \ln \left(\frac{C_{A0}}{C_A} \right) &= kt \\ \Rightarrow C_A &= C_{A0} e^{-kt} \end{aligned}$$

This is the required kinetic equation for first order reaction. So, this equation is common equation and this is a very useful equation for determining the efficacy of any reaction under the head of first order reaction mechanism.

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Interpretation of batch reactor data



Graphs represent the variation of reactant concentration with time and $\ln(C_{A0}/C_A)$ Vs time 't' for first order kinetic irreversible unimolecular reaction.

Levenspiel, O (2006)

So, let us move to the other aspect that is how we can interpret all these kinds of batch reactor data that is here you see that we have represented the two graphs of variation of the reactant concentration with the time So, on the x axis the time factor and the ln, in this the $\ln C_{A0}$ upon C. So, usually it is a straight line or the slope with having the slope k. This gives you the indication of this first order irreversible unimolecular reaction.

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Interpretation of batch reactor data

In terms of conversion the rate of reaction with first-order irreversible and unimolecular reaction, can be written as:

By using the above rate equation & putting the value of C_A in terms of conversion and initial concentration of reactant, we have:

$$\begin{aligned}
 \ln \frac{C_{A0}}{C_A} &= kt \\
 C_A &= C_{A0}(1 - X_A) \\
 \ln \left[\frac{C_{A0}}{C_{A0}(1 - X_A)} \right] &= kt \\
 = -\ln(1 - X_A) &= kt \\
 X_A &= 1 - e^{-kt}
 \end{aligned}$$

It is the equation of reaction for first order kinetics

Now in terms of conversion of rate of reaction with first order irreversible and unimolecular reaction, this can be written as $\ln C_{A0}$ upon $C_A = kt$ and by using the above rate equation putting the values of C_A in terms of conversion and the initial concentration, we may have $C_A = C_{A0}(1 - X_A)$. So, if we utilize these two equations, then we will have $\ln C_{A0}$ upon $C_{A0}(1 - X_A)$ or $-\ln(1 - X_A) = kt$ or $X_A = 1 - e^{-kt}$. Now, it is the rate of reaction in terms of conversion for first order kinetics.

By using the above equation putting the value of C_A in terms of conversion and initial concentration of reactant.

We found:

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

$$\Rightarrow -\ln(1-X_A) = kt \quad \text{or} \quad X_A = 1 - e^{-kt}$$

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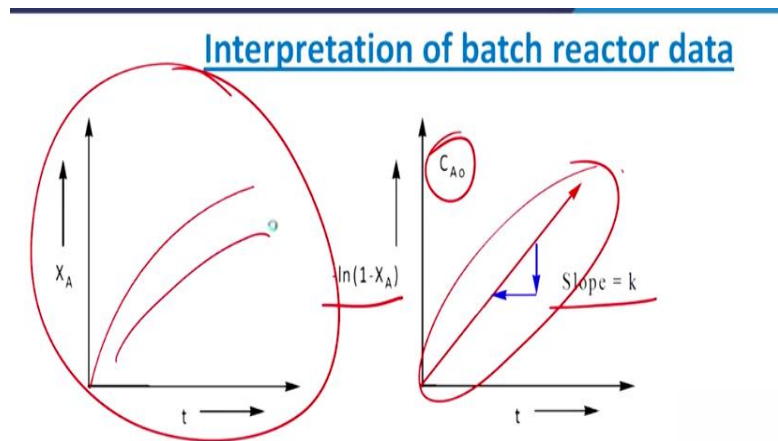


Figure: The graphical representation of conversion variation with time t and $-\ln(1-X_A)$ Vs t .

Levenspiel, O (2006)

Now, again if you try to plot the graphical representation of a conversion variance with the time and $\ln(1-x)$, then you can see that this you will find a straight line. This represents the first order kinetics and this line is having the slope k . This is the C_{A_0} , so with respect to this one. Similarly, you can have this X_A versus t and it gives you the approach of this particular curve.

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Interpretation of batch reactor data

Here, the rate of change of conversion is independent of initial concentration (C_{A0}) i.e.

Now, for time required to achieved full conversion i.e. $X_A = 1$.
[Note]:

So, here we can observe that either time tends to infinite or rate constant tends to infinite. Hence the first order reaction cannot be completed in finite time of interval e.g. radioactive decay.


Now, here if you see that the rate of change of the conversion is independent of any kind of initial concentration C_{A0} . This particular approach is quite useful. Now, if time required to achieve the full conversion say $X_{A0} = 1$.

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rate of change of conversion w.r.t time

$$\frac{dX_A}{dt} = k e^{-kt}$$

for time required for full conversion

$$X_A = 1$$
$$X_A = 1 - e^{-kt}$$
$$e^{-kt} = 0 = e^{-\infty}$$


So, we can represent this equation like now the rate of change of conversion with respect to time that is this one. Now for time required for full conversion, sometimes you may require that how much time is required for the complete conversion that means X_A will be equal to 1. Here, the rate of change of conversion is independent of initial concentration (C_{A0}) i.e.

$$\frac{dX_A}{dt} = k e^{-kt}$$

Now, for time required to achieved full conversion i.e. $X_A = 1$.

$$X_A = 1 - e^{-kt}$$
$$\Rightarrow e^{-kt} = 0 = e^{-\infty}$$

So, in that case $X_A = 1 - e$ to the power $-kt$ or you can write that e to the power $-kt = 0$ or e to the power minus infinity. So, this is the genesis for to evaluate the things with respect to the conversion.

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Interpretation of batch reactor data

➤ **Zero order reaction (n=0)**

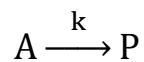
Let us consider the following chemical reaction proceeds with zero order reaction.

$$A \xrightarrow{k} P$$

Rate equation for zero order reaction is independent of concentration of reactant i.e.

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

Now, sometimes you may need to encounter with the zero order reactions. Now zero order reaction as you know that it is represented as $n = 0$. So, let us consider this particular equation A is converting into the product P having the constant k here.



Rate equation for zero order reaction is independent of concentration of reactant.

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

So, rate equation for zero order reaction is independent of the concentration of the reactant and it is represented as $r_A = kdt$, so it is a very small type of thing which is attributed to this one.

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Interpretation of batch reactor data

On rearranging and integrating the above equation, we have:

$$\begin{aligned} - \int_{C_{A0}}^{C_A} dC_A &= \int_0^t R dt & -r_A &= k \cdot \frac{dC_A}{dt} \\ &= C_{A0} - C_A = kt & \text{or } C_A &= C_{A0} - kt \end{aligned}$$

In term of conversion, the above equation can be written as:

$$\begin{aligned} C_{A0} - C_{A0}(1 - X_A) &= kt \\ &= C_{A0} X_A = kt \end{aligned}$$

Now if we rearrange and integrate this equation which we have written previously that is $r_A = k = dC_A - dt$. So, if we try to rearrange and integrate this equation, it will become $C_{A0} - C_A = kt$ or $C_A = C_{A0} - kt$.

On rearranging and integrating the above equation

$$\begin{aligned} - \int_{C_{A0}}^{C_A} dC_A &= \int_0^t k dt \\ \Rightarrow (C_{A0} - C_A) &= kt \\ \Rightarrow C_A &= C_{A0} - kt \end{aligned}$$

Now if we try to write this equation with respect to the terms of conversion, so we can write this equation like $C_{A0} - C_{A0}(1 - X_A) = kt$ or $C_{A0} X_A = kt$. So, we can write like this.

In term of conversion:

$$\begin{aligned} \Rightarrow (C_{A0} - C_{A0}(1 - X_A)) &= kt \\ \Rightarrow C_{A0} X_A &= kt \end{aligned}$$

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Interpretation of batch reactor data

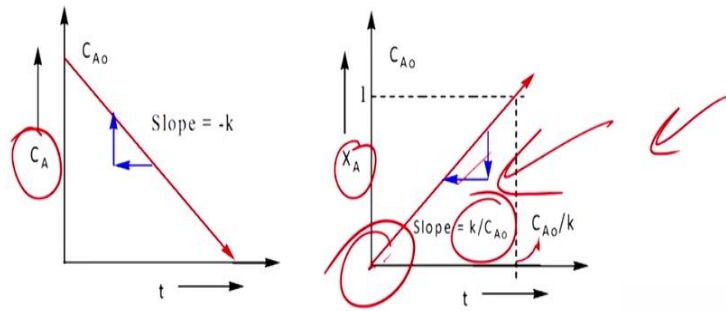


Figure: Plot of variation of reactant concentration 'C_A' and conversion X_A with time 't' for zero order reaction.

Levenspiel, O (2006)

Now, again it is quite obvious that we are having this set of data and we need to put a graph of variation of a reactant concentration C_A and the conversion of say X_A both here and there with respect to time for zero order reaction. And you see that here the reaction is starts at this t t = 0 and it gives you the straight line. This is the slope and the slope is represented as k upon C_{A0}. So, this is the again a very important thing that whenever you have got a set of data, then you need to find out that what is the order of your reaction.

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Interpretation of batch reactor data

The rate of change of conversion with respect to time is given by:

$$\frac{dX_A}{dt} = \frac{k}{C_{A0}} \quad \text{with } t_{\text{end}} \quad \text{for full conversion } X_A \rightarrow 1$$

$$C_{A0} X_A = kt$$

Here, it is clear that the rate of change of conversion is inversely proportional to initial concentration of reactant.

The time required for complete conversion of reactant i.e. X_A = 1 and as the kinetic equation for zero order reaction is:

$$C_{A0} X_A = kt \Rightarrow t = \frac{C_{A0}}{k}$$

Now, sometimes the rate of change of conversion with respect to time is given by this particular equation, equation dX_A upon dt = k upon C_{A0}. This is with respect to the time. Now for full conversion again X_A = 1 and the kinetic equation will become C_{A0} X_A = kt or we can write this for X_A = 1, C_{A0} = kt and this t = C_{A0} upon k. So, this is the equation with respect to the time.

The rate of change of conversion with respect to time is given by:

$$\frac{dX_A}{dt} = \frac{k}{C_{A_0}} \quad (47)$$

Here it is clear that the rate of change of conversion is inversely proportional to initial concentration of reactant.

The time required for complete conversion of reactant i.e., $X_A = 1$ and as the kinetic equation for zero order reaction is:

$$C_{A_0} X_A = kt$$

$$\Rightarrow t = \frac{C_{A_0}}{k}$$

Conditions for kinetics of zero order reaction:

- $(C_{A_0} - C_A) = kt$ for $t < C_{A_0}/k$
- $C_{A_0} = 0$ for $t \geq C_{A_0}/k$, as the concentration of the reactant, can't be negative.

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Interpretation of batch reactor data

Conditions for kinetics of zero order reaction:

- $C_{A_0} - C_A = kt$, for $t < C_{A_0}/k$
- $C_{A_0} = 0$, for $t \geq C_{A_0}/k$, as the concentration of the reactant, can't be negative.

Now, there are various conditions attributed to the kinetics of zero order that is $C_{A_0} - C_A = kt$ for t is less than C_{A_0} upon k , please refer to the graph this graph which we discussed in due course of time and sometimes $C_{A_0} = 0$ for t is greater than equal to C_{A_0} upon k as the concentration of the reactant cannot be negative. This is a very important thing; the concentration of the reactants cannot be negative. That means that reactant try to eat each other that is practically not possible or practically not feasible at all for any kind of reaction.

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Reference

- Levenspiel, O. CHEMICAL REACTION ENGINEERING, Third Edition, John Wiley & Sons, Inc., (2006), ISBN:978-81-265-1000-9.
- Fogler, H. S. Elements of Chemical Reaction Engineering, Third Edition, Pearson Education, Inc., (2002), ISBN: 81-203-2234-7.

Now in this particular chapter, we discussed the interpretation of various concentration versus conversion versus time data and we tried to find out that how we can interpret all those things for the real time reaction. And this particular information is extremely useful for designing of a reactor which is especially useful for the polymerization reaction. And as we discussed that this type of approach and this type of consideration of various parameters are extremely sensitive for the designing of any reactor.

So, the careful consideration is always required for taking these experimental data in due course of time. Now, in case if you wish to have further study of this particular segment, you can look into these references which are enlisted in this particular slide. And by this way, we are summing up this particular reactor design concept and thank you very much for your consideration.