Chemical Reaction Engineering I
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Lecture - 09
Integral Method of Analysis of Batch Reactor Data - Part 2

Welcome to the third lecture of module 3, in this lecture we will discuss the analysis of the batch reactor data, so before going to this let us have brief recap on our previous lecture.

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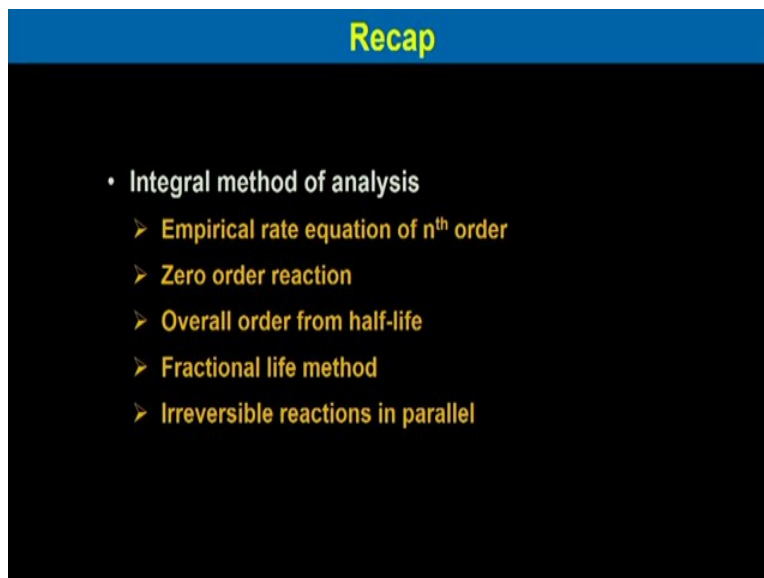
In our previous lecture the following topic we have covered under integral method of analysis, one is we have considered nth order rate equation and we have fitted the data with the experimental results and we found that what is the actual order of the reaction. Then we have considered several other cases, one is zero order reaction where we have seen that rate of the reaction is independent of the concentration of the reactants, then we have considered overall order from the half-life and this half-life method we can consider any fractional life of the reactants. So we have considered then fractional life method and also we have considered irreversible reaction in parallel where we have encountered multiple reactions.

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So as we have started with the multiple reactions in this lecture we will consider again the integral method of analysis for a constant volume batch reactor data, we will consider homogeneous catalyzed reactions. Here also we will see multiple reaction taking place, then we will consider autocatalytic reaction, irreversible reaction in series, first order reversible reaction, second order reversible reactions.
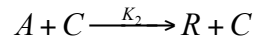
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So, let us consider homogeneous catalyzed reactions. In this case the rate of the reactions will be depend on the un-catalyzed reactions as well as the catalyzed reactions. Let us consider a simple homogeneous catalyzed reaction that is

$$A \xrightarrow{K_1} R$$
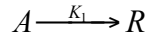
Now, A can also can be react in the presence of catalyst C to form R plus C

$$A + C \xrightarrow{K_2} R + C$$

with a rate constant K_2 here C is the catalyst. So we can write the corresponding rate equations for this elementary reaction we can write

$$-\left(\frac{dC_A}{dt}\right)_1 = K_1 C_A$$

Similarly for the second reactions we can write,

$$-\left(\frac{dC_A}{dt}\right)_2 = K_2 C_A C_C$$

as we can see even if there is no catalyst the reactions will proceed so and in presence of catalysts the reactions again will be faster, so this rate of reactions from the second equations we can see that it is directly proportional to the catalyst concentration.

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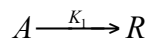
Homogeneous Catalyzed Reactions

Now, let us write the overall disappearance of component A, so we can write for the reactions

$$A \xrightarrow{K_1} R$$

and

$$A + C \xrightarrow{K_2} R + C$$
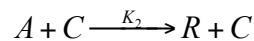
So for this we can write the disappearance of A is

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

this we can write

$$= (K_1 + K_2 C_C) C_A$$

C_C is the catalyst concentration. So if we integrate this relation by integrating we can consider catalyst concentration C_C remains unchanged.

So in that case, if we integrate we can write

$$-\ln \frac{C_A}{C_{A0}} = -\ln(1 - X_A) = (K_1 + K_2 C_C)t$$

So which we can write

$$= k_{observed}t$$

So, how to find out K_1 and K_2 from this relations? So, first what we have to do? We have to run the experiments and we have to plot the concentration profile that means we have to plot concentration versus time and that means if we plot $-\ln\dfrac{C_A}{C_{A0}}$ versus time we will get a straight line passing through the origin, so the slope of this would be $k_{observed}$.

So now, we can plot different $k_{observed}$ versus time, versus concentration of the catalyst. So if we perform the experiment with the different concentration of the catalyst and for each catalyst concentration we can calculate the observed K the rate constant values. So for each catalyst concentration we have rate constant values and if we plot the K observed versus the catalyst concentration we will find that the curve will fit like this with a slope, so slope of this curve is K_2 and this
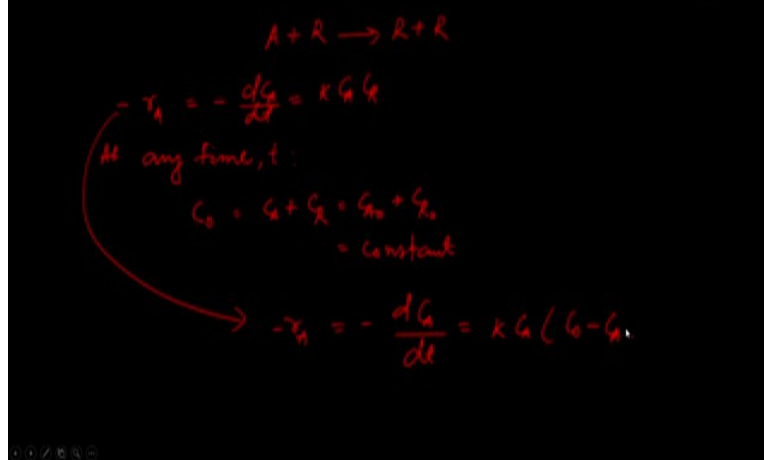
$$k_{observed} = K_1 + K_2 C_C$$

So if we calculate slope K_2 and we can for a particular concentration catalyst concentration we can calculate K_1, this way we can calculate the different rate constants that is K_1 and K_2 for the homogenous catalyzed reaction.

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Now, let us consider autocatalytic reactions, what is autocatalytic reaction? In a reaction in which one of the product of reaction is acts as a catalyst. Let us consider an example of simplest kind. So if we have A as the reactant and which produce R so the product R is reacting with A, so this is the product itself reacting with the reactant and forming the product again.

$$A + R \rightarrow R + R$$
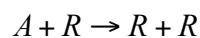
So this is known as the autocatalytic reaction, this is of simple kind.

So if we write the rate of the reaction we can write

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

C_R is the catalyst concentration and C_A is the concentration of A. Now, because the total number of moles A and R will remain constant throughout the reactions, so for any time A and R will remain constant. So with that we can write at any time C_0 is the total concentration would be

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

That means at any moment the total concentration remains constant C_{A0} and C_{R0} is the initial concentration of the reactants and the products.

Now this, if we put this over here our rate equation would be

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

So from here we can calculate $C_R = C_0 - C_A$ and if we substitute this C_R over here so our rate equation would be this.

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Now, we can obtain the integral form of rate equation by integrating the earlier equations. So we have

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Now, if we rearrange it and break down into partial fraction, so rearranging this equation would be

$$\Rightarrow -\frac{dC_A}{C_A(C_0 - C_A)} = kdt$$

Now, if we integrate this we would obtain, so if we first break down into fractions this would be

$$\Rightarrow -\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0}\left[\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right] = kdt$$

Now, if we integrate this we would obtain

$$\ln\frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln\frac{C_R / C_{R0}}{C_A / C_{A0}} = C_0 kt$$

and then we can write C_0 is nothing but the total concentration which was initially present that is

$$= (C_{A0} + C_{R0})kt$$

Now, in terms of conversion if we denote that $M = \dfrac{C_{R0}}{C_{A0}}$ then in terms of the product conversation this equation we can write
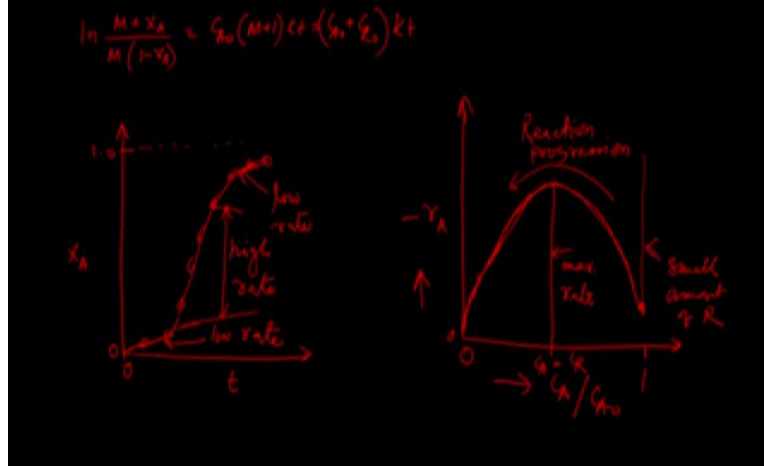
$$\ln\frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)\, kt$$

and then we can write $(C_{A0} + C_{R0})kt$.

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So for autocatalytic reactions, how the concentration and time or rate concentration curves look like? For any autocatalytic reaction to start with initially there must be some product should remain to catalyze the reaction. So we need to have a very small quantity of the starting concentration of the product at the start of the reaction.

Now, as the reactions proceeds the concentration of the product will gradually increase and the concentration of the reactants will fall and at a certain time where the concentration of the products will reach a maxima and that will happen when the reactant concentrations would be equal to the product concentration. After that reactant concentration will fall even if the concentration of the product is higher the rate will fall.

So the concentration time, if we plot this equation

$$\ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)\,kt = (C_{A0} + C_{R0})kt$$

So, if we plot conversion versus time so the conversion can achieve upto one maximum and the conversion versus time curve will look like. So as we can see at the beginning of the reactions the rate of reaction is very low and then in this region from here to this, this region the rate is high and then it fall, so this is low rate again.

Now, if we plot the rate versus concentration it would like this. So rate will start at a very low rate and then it will increase reach a maxima and then it will fall, so this is a starting point because we have started with a high concentration here that is C_{A0} we have started with that is one and taking small amount of R, so the reaction start over here with a initial concentration of C_{A0}.

So than the rate slowly increases and reaches maxima and it is fall down. So the maximum concentration which attains is over here that is means it is $C_A = C_R$. So this is the maximum rate and the reaction progression is like this and so you will get a parabolic profile for the autocatalytic reaction.
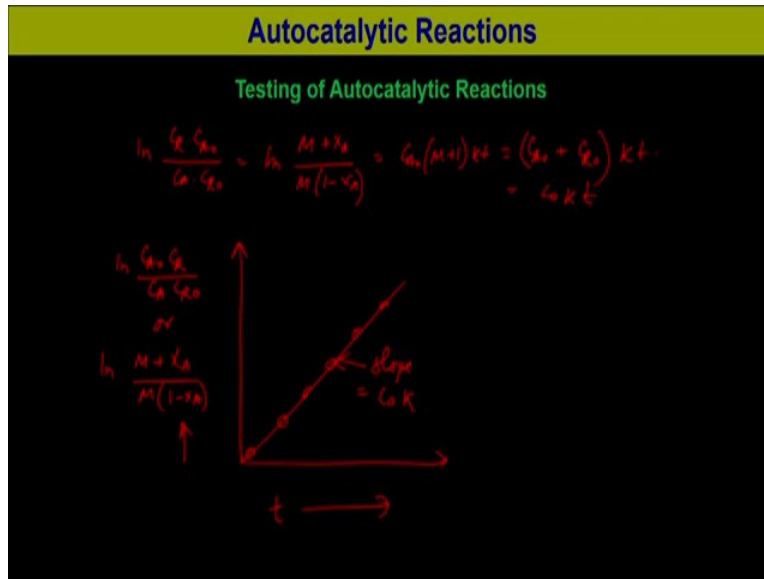
Now, how to tEST the autocatalytic reactions? We take the, we have the equations which is

$$\ln \frac{C_R C_{A0}}{C_A C_{R0}} = \ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)\,kt = (C_{A0} + C_{R0})kt$$

So now, if we plot $\ln \dfrac{C_R C_{A0}}{C_A C_{R0}}$ or $\ln \dfrac{M + X_A}{M(1 - X_A)}$ if we plot versus time and if this gives the straight line passing through the origin then the reaction is autocatalytic in nature with a slope we can calculate which is $C_0 k$. So this way we can notice the autocatalytic reaction.
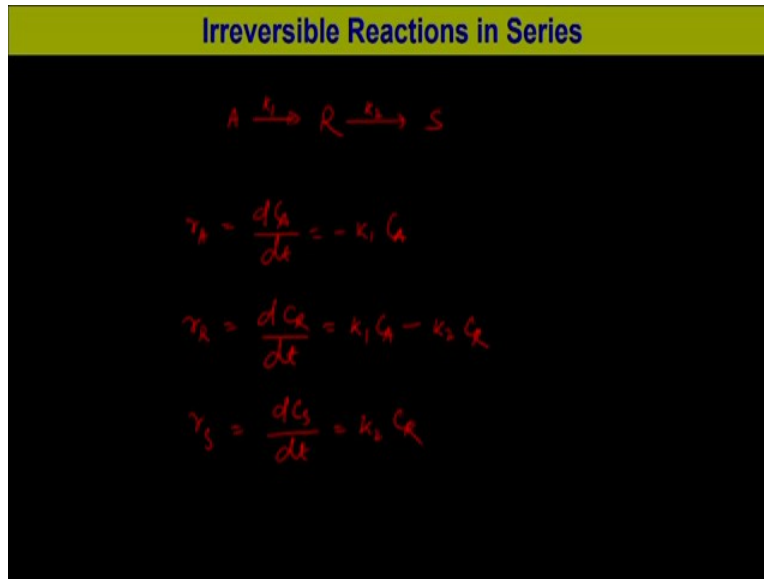
So let us consider irreversible reaction in series, so this we can consider uni-molecular reaction of first order in series. So if we write

$$A \xrightarrow{K_1} R \xrightarrow{K_2} S$$
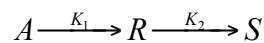
so the reaction reactant A with a rate constant K_1 producing R, R is again dissociating forming S with a rate constant K_2 so this is first order reaction in series, so the rate of the 3 component A, R and S we can write as

$$r_A = \frac{dC_A}{dt} = -K_1 C_A$$

for R which is producing as intermediates we can write

$$r_R = \frac{dC_R}{dt} = K_1 C_A - K_2 C_R$$

for formation of S we can write

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

So now from the first one, first rate of reactions we can calculate the concentration profile of A so let us find the concentration profile of A. So assume the initial concentration of A C_{A0} and we assume that the concentration of R or S initially is zero that means no R or S initially present, so

$$C_{R0} = C_{S0} = 0$$

With this, if we take the rate equations

$$\frac{dC_A}{dt} = -K_1 C_A$$

and if we integrate we would obtain

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

So this is the concentration profile of component A. Now to calculate the concentration profile of R which is also dependent with the concentration of A we have to substitute this concentration in the rate equations of R so let us do that.

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So for R the rate of reaction is

$$\frac{dC_R}{dt} = K_1 C_A - K_2 C_R$$

this we can write

$$\frac{dC_R}{dt} + K_2 C_R = K_1 C_A$$

Now the concentration profile which we have obtain for C_A if we substitute it would be

$$\frac{dC_R}{dt} + K_2 C_R = K_1 C_{A0} e^{-K_1 t}$$

Now, this is the first order linear differential equation. So this is of the form $\frac{dy}{dx} + Py = Q$, so this is of this form.

Now the integrating factor for this form is

$$I.F. = e^{\int Pdx}$$

and the solution of this differential form is

$$y.e^{\int Pdx} = \int Qe^{\int Pdx}dx + \text{constant}$$

So if we apply for this rate form, then the integrating factor, so

$$P = K_2 C_R$$

$$Q = K_1 C_{A0} e^{-K_1 t}$$

So now, if we write the integrating factor would be equal to $e^{\int K_2 dt}$. So this would be equal to

$$I.F. = e^{\int K_2 dt}$$

So for this equation we will have the integrating factor is $K_2 t$.

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Now, if we consider solution of the equation should be

$$C_R e^{\int K_2 dt} = \int K_1 C_{A0} e^{-K_1 t} e^{\int K_2 dt} dt + \text{constant}$$

Now this, if we can simplify this would be

$$= K_1 C_{A0} \int e^{(K_2 - K_1)t} dt + \text{constant}$$

So if we integrate this will be

$$= \frac{K_1 C_{A0}}{K_2 - K_1} e^{(K_2 - K_1)t} + \text{constant}$$

Now, if we apply the conditions at t = 0, we assume that initially $C_R = 0$. So if we apply in this relation we would obtain this side is

$$0 = \frac{K_1 C_{A0}}{K_2 - K_1} + \text{constant}$$

So from here, we can get

$$\Rightarrow \text{constant} = -\frac{K_1 C_{A0}}{K_2 - K_1}$$

So if we substitute in this relation this constant values, then we would obtain

$$C_R = \frac{K_1 C_{A0}}{(K_2 - K_1)e^{K_2 t}} e^{(K_2 - K_1)t} - \frac{K_1 C_{A0}}{(K_2 - K_1)e^{K_2 t}}$$

So if we rearrange this, this will give

$$= \frac{K_1 C_{A0}}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t} \right]$$

which we can write

$$= K_1 C_{A0} \left[\frac{e^{-K_1 t}}{K_2 - K_1} - \frac{e^{-K_2 t}}{K_2 - K_1} \right]$$

so this is the concentration profile for intermediate product which is R.

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Now, we can also, similar way we can find out the concentration profile of S so that we can calculate we know the concentration profile of A and R from the stoichiometry we know that is

$$C_{A0} = C_A + C_R + C_S$$

so we can write

$$C_S = C_{A0} - C_A - C_R$$

So if we substitute we would obtain

$$= C_{A0} \left[1 + \frac{K_2}{K_1 - K_2} e^{-K_1 t} + \frac{K_2}{K_1 - K_2} e^{-K_2 t} \right]$$

So this is how we can obtain the concentration profile of A R and S.

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Now, let us consider different limiting cases. Now if

$$= C_{A0} \left[1 + \frac{K_2}{K_1 - K_2} e^{-K_1 t} + \frac{K_2}{K_1 - K_2} e^{-K_2 t} \right]$$
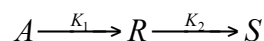
So if we apply two limiting cases, in

Case 1: $K_2 \gg K_1$

So from here we can write

$$C_S = C_{A0}(1 - e^{-K_1 t})$$

So from here we can see if $K_2 \gg K_1$, then this part would be 0 and then from this part, so this will be - K_2 this portion should be approximately equal to - K_2, so in this case it will be $1 - e^{-K_1 t}$. t.

So at a very high rate constant of the second reactions that means from R to S, so we had

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

so if the second reaction is very fast the first reaction will control the overall rate of the reaction. And in Case 2: $K_1 \gg K_2$, similar way we can write

$$C_S = C_{A0}(1 - e^{-K_2 t})$$

that means the slowest step for the series reaction is the second step which will govern the overall rate of the reaction. So in general in a series reaction the slowest step governs the overall rate of the reaction.

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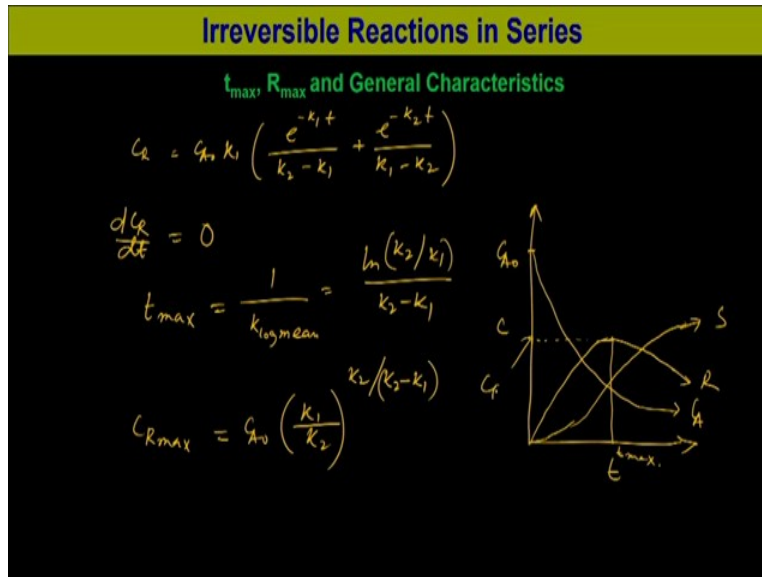
So now, as we have seen that the values of K_1 and K_2 will govern the location of the location and maximum concentration of R that is the intermediate. Now this can be obtained with the differentiation of the concentration profile of R. So concentration profile of R as we derived

$$C_R = K_1 C_{A0} \left[\frac{e^{-K_1 t}}{K_2 - K_1} + \frac{e^{-K_2 t}}{K_2 - K_1} \right]$$

so this is a relation or the concentration profile for R.

Now, if we differentiate this equation and say $\dfrac{dC_R}{dt} = 0$ at maximum, then we would obtain

$$t_{max} = \frac{1}{K_{\log mean}} = \frac{\ln(K_2 / K_1)}{K_2 - K_1}$$

And the maximum concentration we can get if you substitute this t_{max} in this equation we will obtain

$$C_{R max} = C_{A0} \left(\frac{K_1}{K_2} \right)^{\frac{K_2}{K_2 - K_1}}$$

So this way we can calculate the maximum time and the maximum concentration.

Now, how the characteristics curve will look like? So, if we plot concentration versus time we would see that the concentration of A will fall that is C_A we start at C_{A0} and initially there was no R, so R will form and it will reach maxima and then it will decrease. So this is R, then S would also form slowly at the beginning and then concentration of S would increase, so this is for S, so this is the maximum concentration that means $C_{R\max}$, this is $t_{\max}$ and this is $C_{R\max}$.

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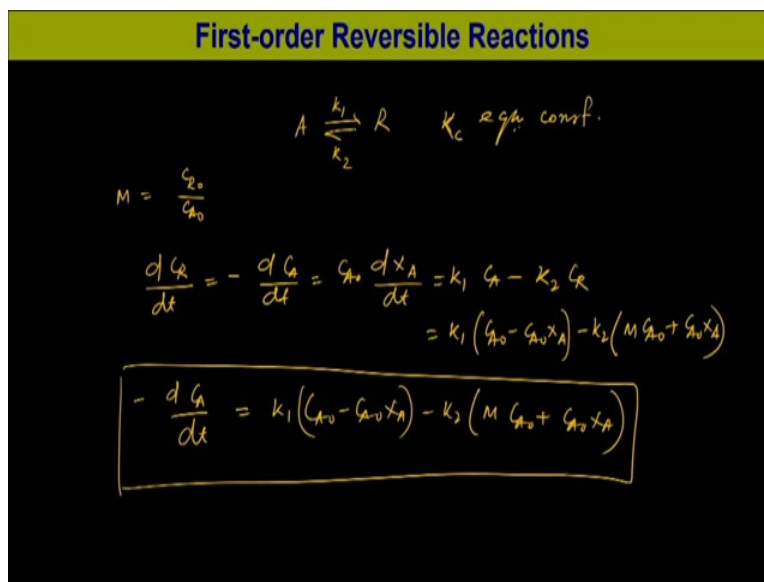
Now, let us consider first order reversible reaction. As we know for most of the chemical reactions are none of the reaction goes to completion and there is really any reaction which is not reversible in nature.

So for reversible reaction, let us consider general reversible reaction of first order which is

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R$$
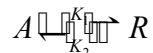
K_C is the equilibrium constant, capital K_C. So this reactions the conversion never goes to completion and if we consider

$$M = \frac{C_{R0}}{C_{A0}}$$

we can write

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = K_1 C_A - K_2 C_R$$

So we can write this is

$$= K_1(C_{A0} - C_{A0}X_A) - K_2(MC_{A0} + C_{A0}X_A)$$

So now, this relation

$$-\frac{dC_A}{dt} = K_1(C_{A0} - C_{A0}X_A) - K_2(MC_{A0} + C_{A0}X_A)$$

this relation if we write at equilibrium the $\frac{dC_A}{dt}$ at equilibrium will be zero.

First-order Reversible Reactions

So at equilibrium $\dfrac{dC_A}{dt} = 0$, so we can write

$$K_1(C_{A0} - C_{A0}X_{Ae}) = K_2(\mathrm{M}\,C_{A0} + C_{A0}X_{Ae})$$

X_{Ae} is the equilibrium conversion minus. So from here we can write

$$\frac{K_1}{K_2} = \frac{\mathrm{M}\,C_{A0} + C_{A0}X_{Ae}}{C_{A0} - C_{A0}X_{Ae}} = \frac{\mathrm{M} + X_{Ae}}{1 - X_{Ae}}$$

so this we can write is

$$K_C = \frac{C_{\mathrm{Re}}}{C_{Ae}} = \frac{\mathrm{M} + X_{Ae}}{1 - X_{Ae}}$$

Now, if we combine these three, this equilibrium ratio that is K_1, K_2 and this one we would obtain let us combine these

$$\frac{dX_A}{dt} = K_1(1 - X_A) - K_2(M + X_A)$$

$$= K_1 \left[(1 - X_A) - \frac{(M + X_A)}{K_1 / K_2} \right]$$

$$= K_1 \left[(1 - X_A) - \frac{(M + X_A)}{K_C} \right]$$

$$= K_1 \left[(1 - X_A) - \frac{(M + X_A)(1 - X_{Ae})}{M + X_{Ae}} \right]$$

So this we can simplify it will be

$$= K_1 \left[\frac{(M + X_{Ae})(1 - X_A) - (M + X_A)(1 - X_{Ae})}{M + X_{Ae}} \right]$$

So if we simplify this, this would be

$$= K_1 \frac{(M+1)}{M+X_{Ae}}(X_{Ae} - X_A)$$

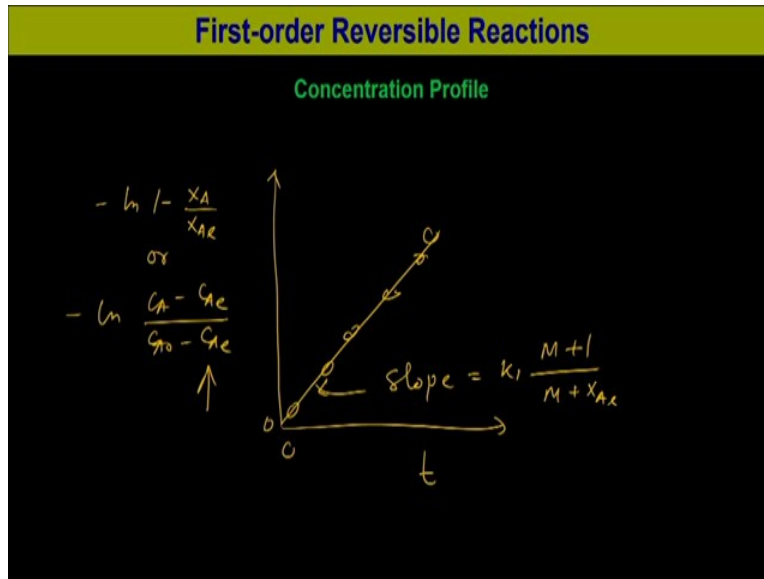so this is that the dX_A equation.

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Now, if we integrate this we would obtain, so our equation is now

$$\frac{dX_A}{dt} = K_1 \frac{(M+1)}{M+X_{Ae}}(X_{Ae} - X_A)$$

So if we integrate with separation of the variable we would get

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M+X_{Ae}}K_1 t \ .$$
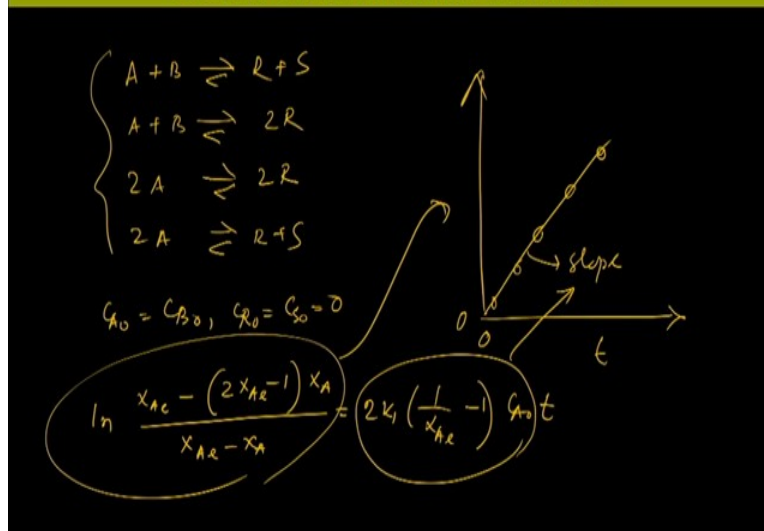
Now, if we plot we will get the concentration profile. So we can plot $-\ln\left(1-\dfrac{X_A}{X_{Ae}}\right)$ or

$-\ln\dfrac{C_A - C_{Ae}}{C_{A0} - C_{Ae}}$, so if we plot this versus time it will give us straight line passing through the
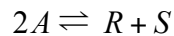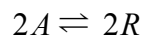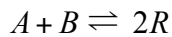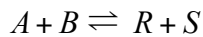
origin, so with a slope would be equal to $\dfrac{M+1}{M+X_{Ae}}K_1$.

Now, for the second order reversible reaction there are different type of second order reversible reactions we can write that is

$$A + B \rightleftharpoons R + S$$
$$A + B \rightleftharpoons 2R$$
$$2A \rightleftharpoons 2R$$
$$2A \rightleftharpoons R + S$$

for all of these if we put the restriction that $C_{A0} = C_{B0}$ and $C_{R0} = C_{S0} = 0$ the integral from of all these rate equation should be same identical. And we can get

$$\ln \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2K_1 \left(\frac{1}{X_{Ae}} - 1 \right) C_{A0} t$$

Now, if we plot this one versus t, so then the rate equations will for that concentration profile will pass through this origin with a slope is equal to this path. So when we go above the second order system the analytical solutions become cumbersome.

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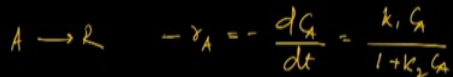
So let us consider reactions with shifting orders. Suppose, if we have

$$A \rightarrow R$$

with a rate of reactions

$$-r_A = -\frac{dC_A}{dt} = \frac{K_1 C_A}{1 + K_2 C_A}$$

Now, if we consider at high C_A concentration that means, this means that $K_2 C_A >> 1$. So in that

case this reaction would follow zero order, so this would be rate would be $-r_A = \dfrac{K_1}{K_2}$, so this will

be zero order.

Similarly, at low concentration of C_A then $K_2 C_A << 1$ than these reactions would be first order

$-r_A = K_1 C_A$, so this behavior we can see if we plot the concentration versus time we can see

initially it will follow zero order upto a certain range and then it follow the first order kinetics.

(Refer Slide Time: 58:48)

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

$$\Rightarrow \quad \frac{C_{A0} - C_A}{\ln(C_{A0} - C_A)} = -\frac{1}{k_1} + \frac{1}{k_2}\left(\frac{t}{\ln(C_{A0}/C_A)}\right)$$

$$\Rightarrow \quad \ln \frac{C_{A0}/C_A}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A}$$

Now, if we apply the integration to the earlier equation we can get the integral form

$$\ln\frac{C_{A0}}{C_A} + K_2(C_{A0} - C_A) = K_1 t$$
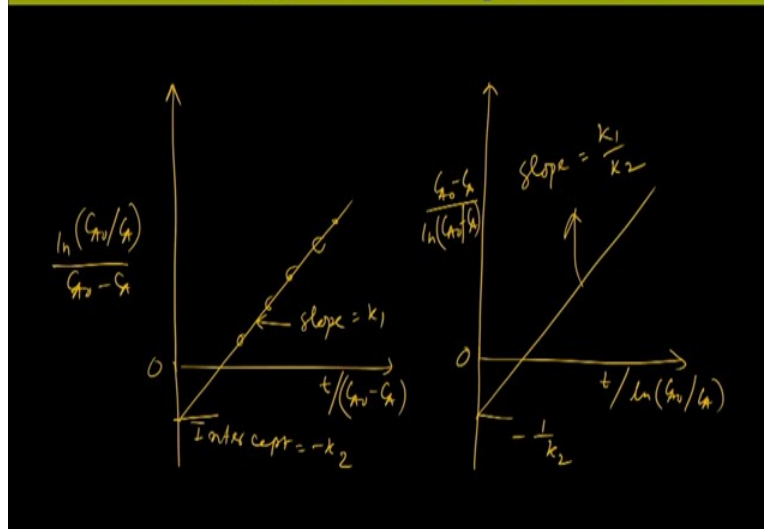
Now, if we linearize this equations, it would be

$$\Rightarrow \frac{C_{A0} - C_A}{\ln(C_{A0} - C_A)} = -\frac{1}{K_1} + \frac{1}{K_2}\left(\frac{t}{\ln(C_{A0} / C_{A0})}\right)$$

or we can write

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

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Reactions with Shifting Order

Now this we can test, this concentration profile in two ways so we can plot $\dfrac{\ln(C_{A0}/C_{A0})}{C_{A0}-C_A}$, then

we will obtain the curve like this, so where the slope is slope is equal to K_1 and intercept is equal

to is equal to $-K_2$ or we can plot $\dfrac{C_{A0}-C_A}{\ln(C_{A0}/C_A)}$ versus $\dfrac{t}{\ln(C_{A0}/C_A)}$. If we plot this we would get

the intercept is $-\dfrac{1}{K_2}$ and the slope is equal to $\dfrac{K_1}{K_2}$, so this way we can test and find out the

values of K_1 and K_2. So thank you for attending this lecture and we will consider the differential

method and the integral method for the variable systems from the next class.