Environment Engineering: Chemical Processes

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Module No # 03
Lecture No # 13

Determination of Kinetic Equations

Hello everyone welcome back to our latest lecture series so I believe we have been looking at some math in previous lecture session. So let us try to take the bigger picture and understand what we have been up to right we have been looking at application of material balances to various reactors the three reactors being batch plug flow and CSTR right and then we applied the particular mass balance equations and two different kinds of scenarios.

So let us summarize them so that you have a picture of what it is that we are up to right so I guess I have a reference equation here which I am going to look at later yes so what have you been up to in general.

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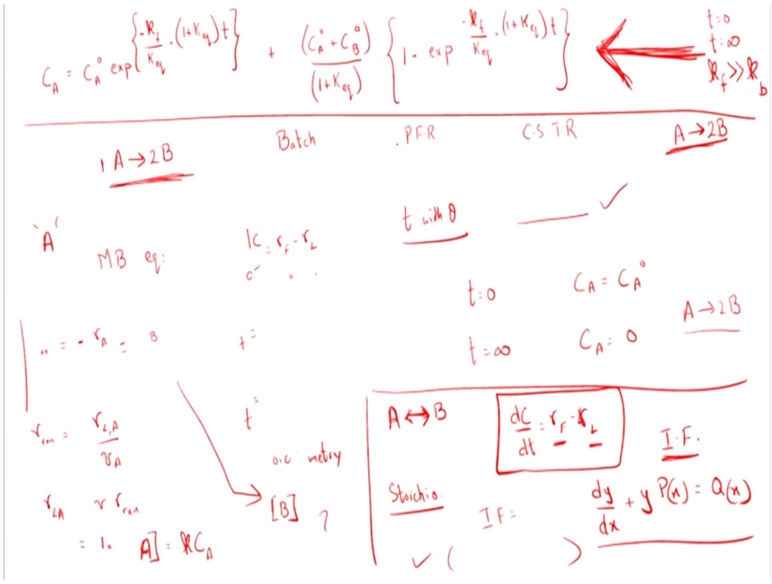

I believe the first example we looked at was an irreversible A goes to 2B if I am not wrong right and then we applied the material balance equation for the batch and what else plug flow and CSTR and how did we do that we identify the compound so I believe initially we did the mass balance or mass balance on compound A right with then wrote down the relevant mass balance equation for example what is it for batch reactor I guess DC / DT = rate of formation of compound = rate of loss.

So we know the relative rates of formation of loss of these compound here what is this compound A? it is not being formed that is 0 and loss is being loss wrote down the relevant equations there. So quickly again how can be relate these particular rates here rate of reaction will be equal to if I am not using the term loss I just going to use to rate of change of A by the stoichiometric coefficient of A then I need to use the term of negative term here right if not I just use to term rate of loss then just going to be rate of loss of A by stoichiometric coefficient of A right and this is what we have.

So rate of loss of A = stoichiometric into rate of coefficient and what is that in this case stoichiometric coefficient of A is 1 right into rate of reaction is rate the constant times the concentration of compound A right I think we also use different nomenclature in this case may be CA and this is what we have when we derive the relevant equation for A and we solve for concentration of A as it changes with time and then we also wanted to calculate how the concentration of B changes with time right.

And did we do that I guess? So for that we applied stoichiometric yes and what did we more or less we try to look at variation of this particular equation here right would be equal to rate of formation of B by the stoichiometric coefficient of B and using the variation here we end up new equation from which we were able to calculate the concentration of compound B as it change with time that is what we did and it is plug flow it is just replacing T with theta and that is what we did it.

And CSTR we had a another equation that we derive right we went ahead and did that so once got that done i believe in each case we also looked at the check is what is the concentration of A when time is that 0 and also time = infinity and obviously when time = 0 we should get CA = CA naught and CA should be = 0 at time = infinity right as A goes to 2B and at infinity right you are going to have all the A being consumed and that is what we believe.

We solve with most of the equation here yes and then we moved ahead and what did we end up by doing I guess we end up looking at an irreversible reaction yes we ended up looking at reversible reaction I am going to summarize here started looking at I guess we looked at reversible reaction here goes to B and B again can transform to A right. So in this case though we are going to have a whenever you write DC / DT = rate of formation – rate of loss right we are going to have both the terms formation loss right.

So thus we have issues with solving this and thus believe once we applied stoichiometric we applied stoichiometric got the relevant equation I believe right and then we use the integrating factor right. And when can we use integrating factor let me refresh my memory divided by DX + Y into function of X = function of another function of X when it is of this form you can use the integrated factor and then we add the relevant solutions for that and we went ahead and solve it right and I believe this is the equation that we end up getting and obviously transformed it with respect to K equilibrium right.

So this is the equation that we end up getting anyway the math involved but that for your understanding I guess obviously you never need to understand the stuff at right you only need to understand the basics their right so this is the equation that we have and again for this case we need to look at we looked at the case when time = 0 when time = I believe infinity right and we also looked at I believe what would be case rate of rate constant of forward reaction is far greater than the rate constant of the backward reaction right.

We looked at that aspect too and what did that give us I guess it give us the answer which was been relatively similar I guess to A goes B or irreversible reaction so this is what we did in the last class and obviously now we are going to continue with this particular session here.

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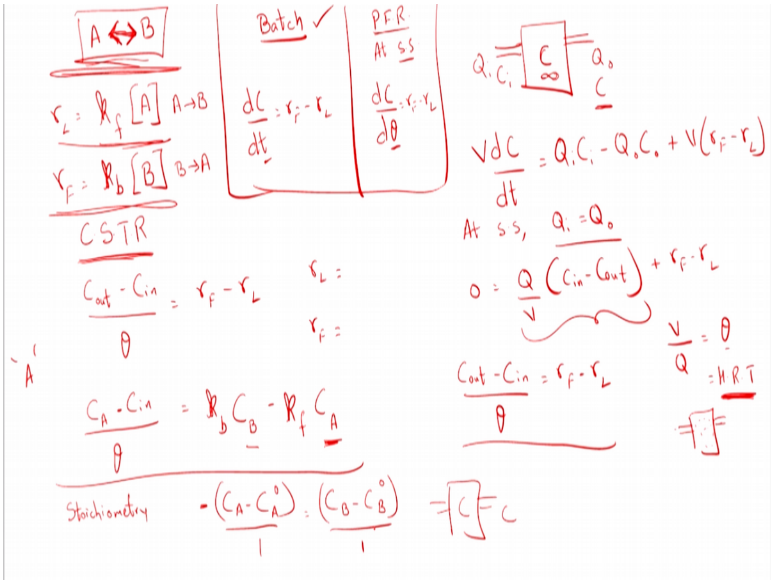

So we are still looking at example of A reversible reaction A going to B and B going to A again so we were done with our enhances with respect to application with respect to batch reactor right so obviously as you know for plug free reactor at steady state what is the only aspect that we changes so if you look at the fundamental equation there that we derived for the batch reactor is the formation – rate of loss DC / DT and here it is DC / D theta = rate of formation – rate of loss.

So obviously we just need to replace time with hydraulic retention time in the case of the plug flow reactor right. So we obviously I am going to go in that in detail here so moving on we have the next case and what is that I guess is the CSTR right so let us look at how to apply the this particular case or CSTR case to your irreversible reaction now. So I am in general we are not good with mugging up formulas.

So let us see again for the purpose of for refreshing our memories too how do we get the mass balance for your particular CSTR again what is the CSTR I continuously stir tank reactor we have flow coming in we have flow going out right and you have the concentration coming in and concentration going out and what is the key here though and the concentration going out is going to be the same as the concentration inside the reactor right and why is that because it is continuously mixed right.

As the system is continuously mixed whatever in the concentration of the compound inside the reactor is going to be the same as concentration that is leaving in the reaction right. So I believe what the mass balance equation right let us look at that VDC/ DT = Q in C in – Q out C out + volume into rate of formation into rate of loss. So at steady state and also assuming that Q in into Q out otherwise the volume is going to change right and what this going to 0 or I am going to divide by volume 2 right 0 = and Q by V into C in – C out + rate of formation – rate of loss.

And what is V/ Q that is theta or the hydraulic retention time right gives you an idea about what is HRT give an idea about gives us an idea about the average time let us say water molecule spends in your reactor right or is time to water molecule spends in your reactor that is given by HRT hydraulic retention time V / Q theta here right where we here again so I am going to win this particular term how to the left hand side.

So I have going to have C out – CN and I guess by theta = rate of formation of compound – the rate of the loss of the compound so I guess we are done with and we are going use that particular equation here C out – C in / theta = rate of formation – rate of loss right so here we are going to apply the mass balance on what is now you are compound number A compound A pardon me and first obviously we need to define the rate of loss and rate of formation.

So what is the rate of loss of your particular compound and rate of formation of particular compound again we need to look at this particular reaction here right so rate of loss of the compound will be equal to rate constant of forward reaction times the concentration of A right rate of loss of the compound and rate of formation of compound is going to be the rate constant of backward reaction of times the concentration of B right because how A being lost when A goes to B and how is A being formed than B goes to A.

So these are the relevant reactions here so let us plug them here please so C out – C in / theta = rate of formation of this particular compound where is that please it is here rate constant KB into concentration of B let us say I am going to use these terms now right – where is the rate of loss here that is here K forward into concentration of A and 1 minor aspect we obviously look at is that this concentration of A is going to be = this variable C out right because as we just discussed whatever it is inside the reactor will be the same as the one going out of the reactor right.

So I am going to modify that so C or concentration of A – C naught or C N by theta = KB CB – KF into CA so this is where we are and what have been doing up to I guess we cannot solve this equation because we have two independent variable here CB and CA right and CN is the known value of the initial concentration of known value so what do we do we look again look at stoichiometry right and what is that I guess I CA naught or CN stoichiometry coefficient 1 will be equal to CB – CB naught right by the stoichiometric coefficient again one.

So this is what we have and so let us try to write this down or the fresh sheet of the board and then take this through.

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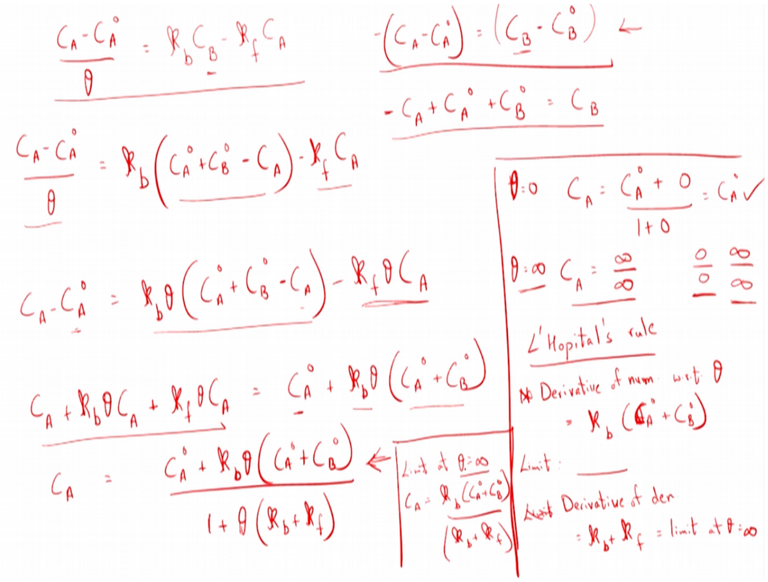

$$\frac{C_A - C_A^0}{\theta} = k_b C_B - k_f C_A$$

$$-(C_A - C_A^0) = (C_B - C_B^0) \leftarrow$$

$$-C_A + C_A^0 + C_B^0 = C_B$$

$$\frac{C_A - C_A^0}{\theta} = k_b(C_A^0 + C_B^0 - C_A) - k_f C_A$$

$$C_A - C_A^0 = k_b\theta(C_A^0 + C_B^0 - C_A) - k_f\theta C_A$$

$$C_A + k_b\theta C_A + k_f\theta C_A = C_A^0 + k_b\theta(C_A^0 + C_B^0)$$

$$C_A = \frac{C_A^0 + k_b\theta(C_A^0 + C_B^0)}{1 + \theta(k_b + k_f)} \leftarrow$$

Limit at $\theta = \infty$

$$C_A = \frac{k_b(C_A^0 + C_B^0)}{(k_b + k_f)}$$

$$\theta = 0 \quad C_A = \frac{C_A^0 + 0}{1 + 0} = C_A^0 \checkmark$$

$$\theta = \infty \quad C_A = \frac{\infty}{\infty} \qquad \frac{0}{0} \quad \frac{\infty}{\infty}$$

L'Hopital's rule

Derivative of num. w.r.t. θ

$= k_b(C_A^0 + C_B^0)$

Limit:

~~Limit~~ Derivative of den

$= k_b + k_f =$ limit at $\theta = \infty$

So CA – CA naught / theta = KB CB – KF concentration of A what is the stoichiometric – of CA – CA naught = obviously going to be = CB – CB naught so let us try to transform this and solve for our particular equation so what I need to calculate I need to calculate CB so CB is going to be – CA + CA naught right + CB naught let us see if I am made any mistakes please CB I just took this CB naught turn to the left hand side and open up the brackets – CA and + CA naught looks like on the right track right.

So again we substitute that CA – CA naught by theta = the rate constant of backward reaction times this particular term and what is that CA naught + CB naught – CA right – rate constant of forward reaction times the concentration of BI in the reactor right and let us try to solve for this I guess right CA – CA naught = KB into theta into CA naught + CB naught – CA – KF theta CA right.

So if I am trying to bring all the term with respect to CA with left hand side and the other term to the right side so CA is going to be here and where are the other CA terms + KB theta CA and again + KF theta CA is going to be = CA naught right + KB theta into CA naught + CB naught right and then obviously solving for CA what is that going to end up with I guess CA is going to be equal to CA + KB theta and CA naught + CB naught / and what else we have here 1 + theta into KB + KF let us review what we have been up to.

So this equation from stoichiometric right change in A and change in B relating that here and I believe we substitute that in our basic mass balance basic equation right and that is that we see here CB = CB naught CA naught and – CA that is what we just did here and we still have the other terms and transforming that in taking theta to the right hand side CA – CA naught = KB into theta CA naught + CB naught – CA – KF theta into CA.

Again what do we say transforming the equation such that we all the terms with respect to CA on the left hand side we have CA + KB theta into CA right again + KF theta into CA = CA naught taking this term to the right hand side + KB theta into CB naught + CB naught and here I guess we have CA = CA naught + KB theta + CA naught into CB naught by 1 + theta into KB + KF we have this.

So now need to do our check again and what are all usual checks we check when time is at 0 what is our situation so how does this equation transform into when time = 0 CA = CA naught + not time pardon me here it is hydraulic retention time right when theta = 0 CA naught + as theta = 0 + 0 / 1 + 0 that is = CA naught that check and we are done with that right and what is the case when theta = infinity.

So let us see what happens there so CA = CA naught + okay now we have a unique situation here we have infinity / infinity right. SO how do we go about solving this I guess let us here whenever we have this particular situation when you are trying to look at the limit of a particular what we say equation and you have it in the form of either 0 / 0 or infinity / infinity.

So we are going to consider the hoptial’s rule right and we consider the hospital rule obviously when we are trying to look at the limit of particular variable and we are ending up with 0/0 or infinity / infinity so I believe we discussed that we need to look at the derivative of numerator and denominator with respect to the relevant variable so here I am going to write down derivative of numerator and that is = what now what is the numerator here is CA naught + KB theta into CA naught this is the numerator here.

So derivative with respect to theta will leave us with respect to theta will leave us with KB into CA naught + CB naught right and derivative and what is the limit I guess what is the limit of numerator once we have taken the derivative and that is going to be the same case here and as we apply theta = infinity that is the same case here and what I the limit not limit pardon me derivative of the denominator with respect to theta that is going to be KB + KF right and that again is the limit at the infinity 2 at theta = infinity.

So let us see what do we have here now I am going to continue this here for sake of our understanding so what do we have here we have the limit at theta = infinity for CA is going to be equal to KB into CA naught + CB naught right / KB + KF so this is our particular concentration of A at obviously at equilibrium I guess or at theta = infinity. So let us try to work out one other particular set and then move on so I need to rewrite this particular equation in the next board I guess right.

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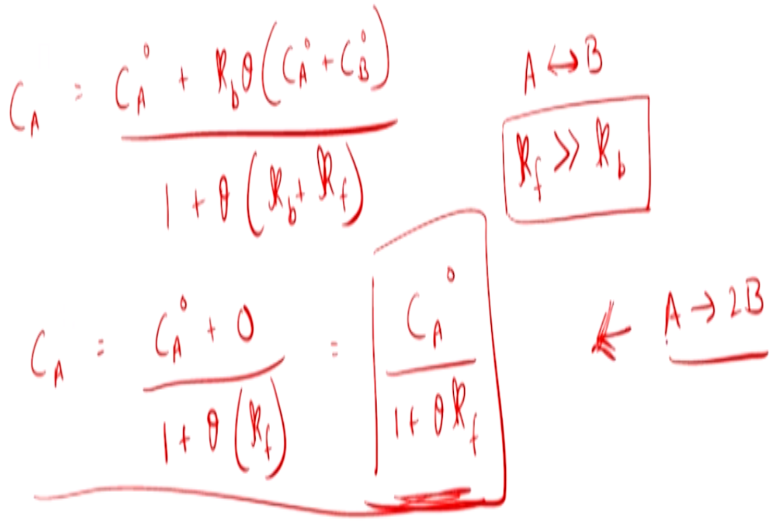

$$C_A = \frac{C_A^0 + k_b\theta(C_A^0 + C_B^0)}{1+\theta(k_b+k_f)}$$

$A \leftrightarrow B$

$\boxed{k_f \gg k_b}$

$$C_A = \frac{C_A^0 + 0}{1+\theta(k_f)} = \boxed{\frac{C_A^0}{1+\theta k_f}}$$

$\leftarrow A \to 2B$

So it is equal to CA = CA naught + KB time theta into CA naught + CB naught / 1 + theta into KB + KF I believe right and so the next aspect that we are going to look at obviously is that when it is a irreversible reaction let us say we are now considering A goes to B and so on and B goes to A again so (()) (21:20) irreversible reaction what does that mean that the K forward reaction is going to be far greater than the K backward reaction right.

So let us see what we are going to have in that case I guess so it is going to be CA = CA naught + let us say may be can I call this 0 1 + theta into KB + KF just be KF right so that is going to be = CA naught by 1 + theta into KF right so if we look at what are the case was for our irreversible reaction A geos to 2B it should be relatively similar to what we just derived right.

So we now looked at the specific A when K forward is far greater than K backward yes and with that we ended with our particular case and you know try to look at the situation and we end with set of variable more or less same as we with respect to our example when we looked at the irreversible case of A goes to 2B right so we now we will move on to the last aspect right in kinetics and the next aspect I guess the major aspect we are going to discuss after this session is going to acid and base.

But before we move on to acid and base relevant chemical process we are going to have the wrap up the aspect with respect to determine let us say rate equations as in the practical relevance let us say we conducted some experiments and with the respect time let us say we have the data with respect to our of concentration let us say right and let us say you do not have the relevant knowledge about what is the form of the equation and in what is the mathematical what do we say equation that would best represent in this particular data now right.

Or you do not know which particular order it is that the of the reaction I guess so how do you go about though the aspect let us say how do you use the data able to come up with your form if your particular equation now right and also when you come up with the form of equation let us say you also rarely will have the relevant rate constant let us say right or how did you go about calculating relevant rate constant or your observe rate constant let us say.

From the give data now right so this is what we are going to discuss from particular example but we are going to obviously have a brief what it is going to be up to right.

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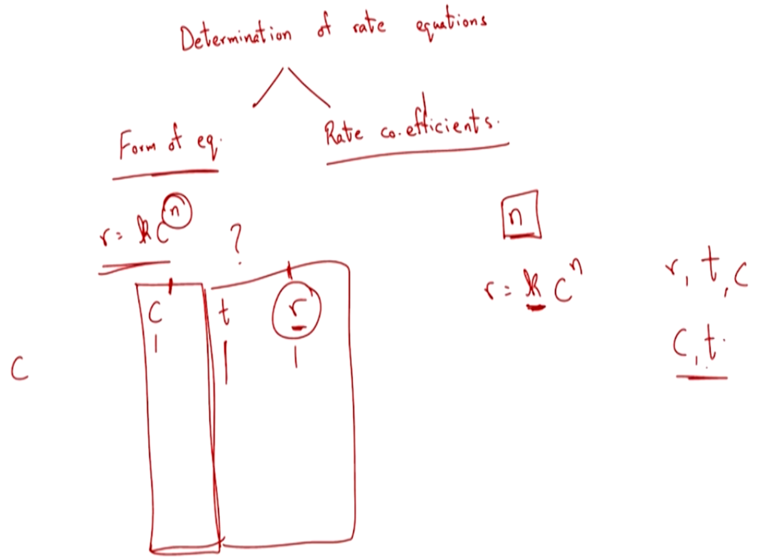

So here we are going to talk about determination of rate equation of rate equation and this context we have two aspects right one would be let us say determining the form of the equation or the reaction let us say write and the second one would be determining the rate coefficient let us say so let us say we are going to obviously look at the example in relation to what we are up to here.

But again keep in mind that we are looking at a particular case we have concentration versus time data or particular experiment let us say either you observe out their at nature or something that cannot read in the lab right and then you are trying to let us say do into have the enough what do we say background let us say or there is nothing available in the literature let us say that is guess what is the order of this particular reaction is going to be let us say right.

Then how are you able to come up with your particular what do we say order now right so you are going to try to fit various models right then your particular data and then look at which model would be the best fit and from that obviously would be able to look at your particular form of the reaction of the equation right and then obviously let us say you know the example I guess I have something relevant to R = KC to the power N right and now what I am talking about is let us say I do not know order of this particular reaction let us say how do I do that.

So i have concentration versus time data and going to let us say modify this into such a way that I have concentration or you know now I need rate versus time data going to come with the day to be able to calculate rate and how do I calculate rate let us say right I depends obviously upon what reactor or the system it is I guess right so if it is batch reactor and it is only first order loss.

So rate would then as we are going to look at going to be similar to or equal to – DC / DT if it let us say what is this now CSTR or completely mixed flow reactor is going to be the DC / D theta right not DC / D theta that for a plug flow reaction I guess right and then obviously for the again the CSTR you have the relevant equation but obviously it is not a differential equation I guess right.

So depending upon the type of reactor we can come up with relevant rate and then form modify the relevant data so that you can now have instead of concentration versus time you will now be able to calculate rate and the relevant time right and then you can fed this particular data let us say or you know in this case looks like in this equation obviously it is rate versus concentration I can fit this particular rate and what do we say concentration or I can fit the model pardon me to the data right and they get the form of the equation by looking at let us say which particular what do we say values give me the best fit right so that is one aspect right.

And let us say once I do that let us say I can now what do we say now order of reaction let us say right then I can round this off to the relevant order right and then be able to more accurately value of my K here right. So again there is two approaches they do rate versus time right or rate versus concentration of approach or I can do the concentration versus time approach right. So again this aspect I guess obviously you would hopefully be clearer when we look at the relevant example.

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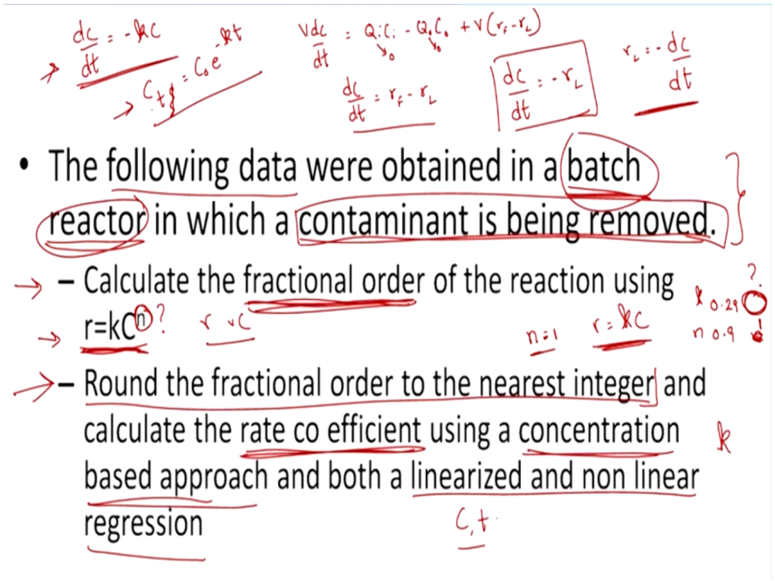
$\frac{dc}{dt} = -kC$ $C_t = C_0 e^{-kt}$

$V\frac{dc}{dt} = Q_i C_i - Q_0 C_0 + V(r_f - r_L)$

$\frac{dc}{dt} = r_f - r_L$ $\boxed{\frac{dc}{dt} = -r_L}$ $r_L = -\frac{dc}{dt}$

- The following data were obtained in a batch reactor in which a contaminant is being removed.
  - Calculate the fractional order of the reaction using $r=kC^{n}$? $r \propto C$ $n=1$ $r = kC$ k 0.29 n 0.9
  - Round the fractional order to the nearest integer and calculate the rate co efficient using a concentration based approach and both a linearized and non linear regression k C, t

So let us look at example that we have so looks like we have some data right in a batch reactor the key is that you know from batch reactor and which the contaminant is removed let us say the key is that is being removed let us say right so before we go further let us apply the mass balance right so we know the generic form of the mass balance let us apply that here right what do we know VDC / DT right = Q in C in – Q out C out + volume into rate of formation – rate of loss right.

But here obviously it is a batch reactor right batch reactor Q in C in and A out C out would be 0 there is no flow coming in or going out right and now I am just left with DC / DT = - rate of loss right or rate of that loss = - DC / DT right. So this is the key that we have understand or you know or we need to be able to (()) (28:32) I guess from the particular scenario here right again it obviously depends upon the kind of reactor and scenario in each case right.

And so the first aspect which we are going to look at is let us say you know if we are trying to fix the moral to equation similar to this rate equation let us say right and I want to though now be able to calculate fractional order of reaction as in what is this N now I do not know what is this fees I just have the data for concentration and time.

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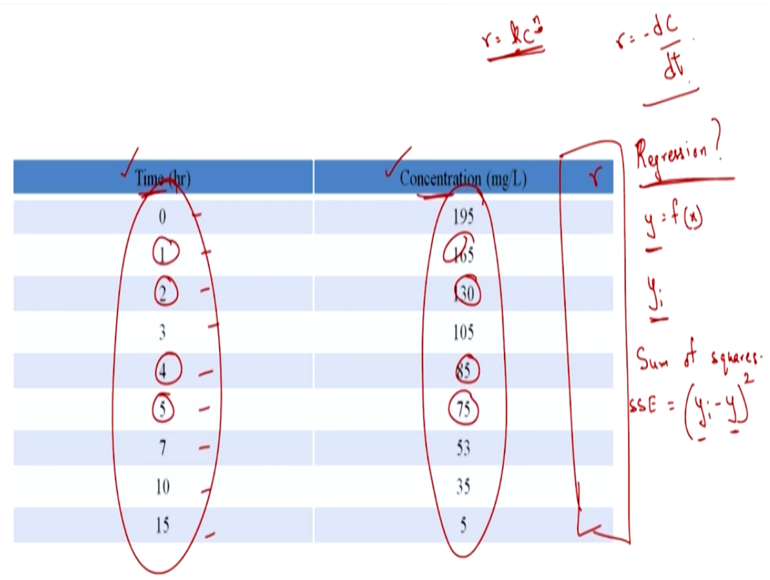

$r = kc^n$

$r = -\frac{dC}{dt}$

Time (hr)	Concentration (mg/L)	r
0	195	
1	165	
2	130	
3	105	
4	85	
5	75	
7	53	
10	35	
15	5	

Regression?

$y = f(x)$

y_i

Sum of squares.

$SSE = (y_i - y)^2$

So this is the data that have time in hours and concentration of milligram per liter right so but I need to be able to calculate order of that particular reaction let us say right so now how do I go about that now right so that different ways so if you had sufficient background or let us say if you were able to find relevant literature you can obviously find the order of the reaction from that particular literature right available literature but if not what can you do you are going to let us say conduct regression right.

So here obviously a new term you are going to look at what it is you are going to conduct regression or you know what I this mean you are going to fit what do we say look for the model and best fits this date of time versus concentration and from that we could be able to calculate the value of N I guess. So I would I fit to my model to this particular model R = KC to the power of N now right.

So there are different ways as we are looking at a approximation I can look at any two data's sets let us say and then you know manipulated or substitute get some value of K and some value of N right but obviously some issue when this such an approach is that right you are not considering all the data now as in our experimental value or your experimental determine value will have as a analytical error or you know errors due to the what do we say analyst itself I guess right due to working of the analyst let us say there are many error can crepe in right.

So to take that into account the best approach obviously you would like to look at a approach that would consider all the date set right so in that case we are going to look at regression I guess right and how do we go about that right the approach is obviously to look at the model that would best fit the data now right. So as in have what do we say why as the function of X right this is actual value or true value.

So let us say I come up with my model value let us say YI let us say right what would be the model be able to predict right values that would be similar let us say or would be the best fit I guess right for particular experimental value that is the key here.

So approach here more or less that you will minimize the sum of squares some of squares and what is that some of square error it is the sum of square error I guess some of squared error = obviously nothing but the model value of the error I guess right between the model and the actual value raise to the power of 2 right. Again calculating the error right and those values which will minimize this error let us say would be would confirm the best fit model right so that is the key.

But obviously we could have just looked at attitude and why are we taking this square one aspect is that error can be positive or negative suitable to be able to rule that out to take that into account and squaring it but that can also be done looking at the magnitude right but we look at the square so that I guess or we consider square let us say because you want to look at the or give enough weightage to the out layers too right anyway let us look at the example now what do we have here.

I have to calculate the fractional order of the reaction using R = KC / RN or KC to power of N I know that RN = DC by DT now right. So because my equation is R versus C right I need to be able to garner or gather data right as in here I have only time and concentration but model is R = KC to the power of 10. So I need to come up with the rate let us say but each of these particular sampling time I guess so how do I able to calculate that as we just looked at it at the previous slide it is going to be equal to – DC / DT right.

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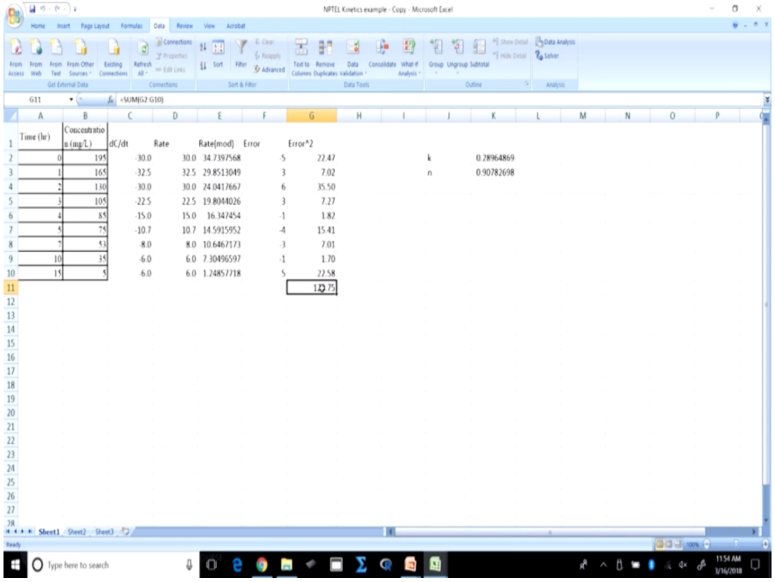


G11 =SUM(G2:G10)

	A	B	C	D	E	F	G	H	I	J	K
1	Time (hr)	Concentration (mg/L)	dC/dt	Rate	Rate(mod)	Error	Error^2				
2	0	195	-30.0	30.0	34.7397568	-5	22.47			k	0.28964869
3	1	165	-32.5	32.5	29.8513049	3	7.02			n	0.90782698
4	2	130	-30.0	30.0	24.0417667	6	35.50				
5	3	105	-22.5	22.5	19.8044026	3	7.27				
6	4	85	-15.0	15.0	16.347454	-1	1.82				
7	5	75	-10.7	10.7	14.5915952	-4	15.41				
8	7	53	-8.0	8.0	10.6467173	-3	7.01				
9	10	35	-6.0	6.0	7.30496597	-1	1.70				
10	15	5	-6.0	6.0	1.24857718	5	22.58				
11							1[illegible].75				

So let us switch over the excel and get this done right okay here I guess said some stuff out now I am going to calculate the rate so it is going to be equal to so this particular so here I guess I have different data points right and obviously I need to look at what do we say difference DC / DT so here I am going to look at numerical difference obviously right so it is going to be = bracket and so I am going to look at the difference of obviously I guess right.

So it is going to be the forward differential here this – this and bracket close divided by again bracket start right – this and bracket close right so what do we have here we just calculated by different DC / DT I guess right. So this particular C2 – C1 right by T2 – T1 that is what I have here so enter and but I should not get this done.

What do we say just give the same forward differential method for all the other what we say data points in general forward or backward differential which we are going to look at let us say will lead to compounding of the errors I guess right here we are going to have to calculate DC / DT and we are going to obviously look at the numerical differential delta T / Delta A but the key here is that obviously because of lack of data we are going to for the extreme cases right at time = 0 and time = 15 for the backward and forward and backward differential respectively.

But in general if you look at the taylors (()) (34:21) look at the relevant error I guess right you will see that central differential is relatively better right. So let us look at the central differential for this I guess = so bracket – bracket close divided bracket close and enter so what have to done here we looked in the central difference as if with respect to time = 1 I looked at concentration of time = 2 – let us say the one at time = 0 IT2 – T0 I guess right.

So enter so I am going to try to copy this the same what do we say here right so then this is what we have here and enter please for last cell obviously we know we do not have enough data to be able to look at the what do we say this central differential right or central differential. So i am going to delete this itself and delete and so it is going to be equal to instead of central differential I am obviously going to look at backward differential here right.

So that is going to be equal to bracket start this – this divided by – enter okay now for these data sets right data points anyway I looked at forward and backward differential and for all these data sets right I looked at central differential right. So again here the DT /DC is negative so obviously as we calculate earlier rate = - DC / DT so that is going to be equal to -1, 1 into enter.

So the rate I guess right I have the same here and now let us say what I need to do here now I have the rate yes I need to be able to calculate model value of rate so what is the approach here I am going to let us say (()) (36:31) you can understand I guess so I need to supply some initial value for the Constance of what is this now K and M right.

So I am going to supply some initial value of K and M right for the rate constant then the order right and then be able to calculate the model rate so for N let us say I stand with 2 enter and for K let us say start with .5 right and obviously hopefully at least within the range of the expected value anyway otherwise solver is going to have what we say difficult in getting that right so that is = to now so what is my rate model here right.

So let me go back to our particular slide view right and let us see where we are here rate = KC to the power of N right so it is going to be equal to this cell into and the concentration here C to the power of N is out here right enter and obviously I can cannot drop this right but obviously if I do so right you know I am going to get an error because I cannot do so it is going to use to successive cells so I need to keep this relevant cells or K and N values or cells constant.

So K here is K2 dollar symbol and again dollar symbol and for also the N value N cell corresponds to N dollar symbol and again one second please dollar symbol enter and so now let us see where we end up with okay and now you see this cell does not change but one correspond to C changes right.

So I am keeping these cells relevant to this rate constant in order the same enter so I can calculate the error that is equal to the what do we say the actual rate right – the model rate and enter. And let us say now I need to just be able to drag draw this right and this square of the error = bracket I guess okay bracket close to power of 2 and enter right and now I need to be able to calculate the some of squared error some of all these errors so that is going to be equal to sum of this and enter right.

So now i have sum of squared errors calculated for a trail value of the 2 variables that we are trying to find the two variables are K and N so I started with trail value of point and 2 right and then I calculated the sum of squared errors right. Error how did we calculate that just be doing the actual rate the error or the difference between the actual rate that we measure let us say right and the model rate based on the relevant constant that you choose as a trial right.

So here I guess we are going to look at data analysis right data and then go to solver right so excel as this particular add on let us say right if you do not have this particular add on you can just go to options in excel and then add in and then add this solver in data analysis tool track right if you do not have this install I guess right.

And how does this help us now so here I have some of value for some of squared error for a particular value of this two variables which are rate constant and order right. So solver let us say help me in let us say changing in or try a going by error guess changing the value of K and N and that this some of squared error is going to be minimum right.

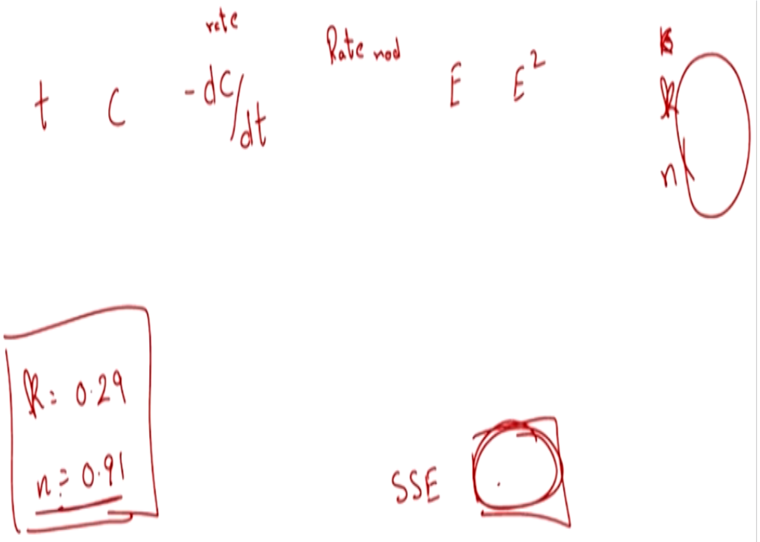
So let us look at that I guess the target cell I guess is going to have to be G11 so that is set and I want to have minimum let set right the value need to be minimum it can be by changing which cells by changing K and N cell right so let us say solve so okay I guess we solve for it and I came up with some particular solution here but because let us say my initial values of way to half I guess right looks like I have relevant what do we say (()) (40:53) values try it out with what do we say new set of values I guess right because I know that K cannot be negative right.

So there are many aspects let us go to be 0.5 okay and let us say N to be around let us say 1 right and now let us run solver again so that you know I am starting with trial value now right earlier I guess solver have a issues right converging on solution but you do know that the rate constant cannot be negative right. So here again trying to assist this solver and arriving at the solution right I get converging at the solution right.

So I am choosing values let us say which now let us say have a smaller some of squared errors right so the closer you start the true value the easier it is for solver to be able to solve this so I am going to repeat that right and I guess everything else is going to be set right okay and I am going to say solve and I guess now I have the relevant values. So now you see that the sum of squared errors is the minimum it can be 120.8 I guess and for which values is it minimum looks like values of K to be 0.28 to 29 N value of 0.91 right.

So I guess here we have done with first part of our question let us go back to question again right so what does it ask us to calculate the fractional order of the reaction using R = KC to the power of N and so how did you go about that.

(Refer Slide Time: 42:19)



We had time and concentration we calculated what do we say DC or – DC / DT right which is the rate and then we calculated the rate model right and how did we do that by assuming some value of rate constant and fraction order let us say or order of the reaction we calculated that we calculated the error square and then calculated the sum of these squared errors right.

And then we asked excel to change the values of K and N to be able to minimize the values of some of squared errors right so from that what values have arrived so K we arrived at to be 0.29 K have 0.29 and N to be 0.91 I guess right so in general I guess this is the experimental observe fraction order but you know that theoretical values usually their integers let us say right obviously I need to round it off right.

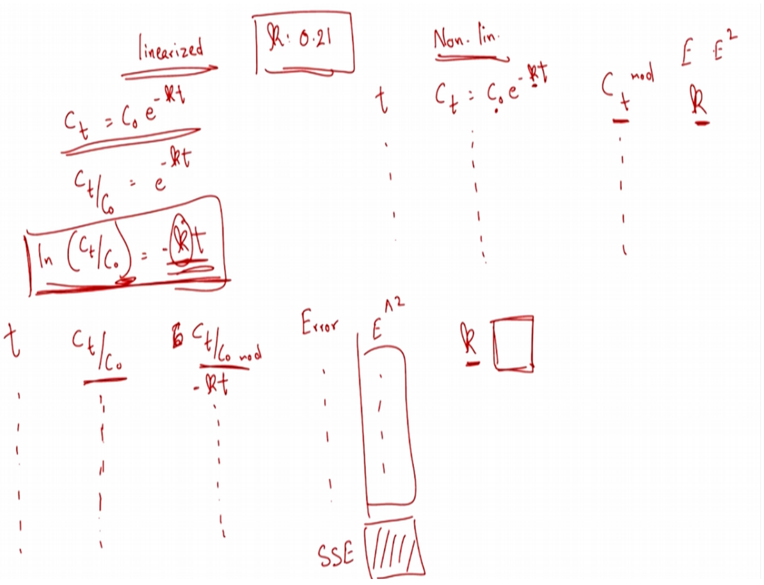
So the theatrical value should be 1 I guess right so let us the second aspect now and look at how to go about that right and second aspect I guess is you know obviously we need to round fraction order to the nearest integer right that I what we need here now the N or order =1 right so what is the rate equation R = KC right so this is what we have now right to the nearest integer and calculate the rate coefficient.

So now that i change the value of N I mean we have I guess K value we got to be 0.29 and N to be around 0.9 right but now I am changing value to what would be a reasonable value right and I know should be 1 right if it is near about 0.9 and now what is now the value of K right that will again be or you know are we to the best feed model again right so that is something I need to do now right but the question I guess what is this ask us to do.

It again ask us to calculate the rate coefficient of the rate constant K using a concentrating based approach not R versus C, C versus let us say time and also I guess we have two aspects to look at linearized and non-linear regression I guess right. So let us look at what it is that we need to consider I guess right. So before we go further I guess we need to understand that the form of this equation is DC / DT = - rate of loss right so to be able to look at the concentration based approach obviously I need to modify my particular equation here.

So DC / DT = - rate of loss but from my particular calculations so now it is = KC right so that is equal to – KC right and for this I guess we know that the I solve for this from 0 to T it is going to be = CT = C naught into e power –KT right and why is that again this is the batch reactor and from my calculation that I know that the CT not solve that I guess you know we did look at the relevant case earlier to and it is straight forward to the solution would be after integration CT = C naught into E power – KT.

(Refer Slide Time: 45:35)



So here now we have two approached to consider right so one is asking for the linearized approach right and the other for the non-linearized approach right linearized as in now CT = C naught into E power 0- KT this is into form of my particular equation so I guess regression there are different ways right you can transform this equation to make it linear so how can I do that let us say I know CT by C naught = E power – KT right so now natural logarithm of CT / C naught = - KT.

So now it is linearized and I can conduct the regression on these aspects I guess right so what would I connect the regression on I would conduct the regression on let us say CT / C naught and 1 particular set of data and time and one particular set of data right and I am going to repeat the same approach right calculating the error and so on and hence so forth and then I guess I will calculate the what do you say CT / C naught model right for which how would I do that I need to assume some value of K right it is going to be equal to – KT right.

And I have time here so I can calculate the mode value of CT / C naught right I need to obviously for that assume the value of K so I am going to go ahead with that so once I have the true CT / C naught and what we say moral value of CT / C naught I can then calculate the error or the difference between them right and then the square of the error right and then I will calculate again the sum of squared errors right the sum of all these squares and then again what am I going to do?

I am going to ask solve right to let us say minimized this particular sum of squared errors right this particular cell by changing this cell of K right so again let us go ahead with that approach here and let us say I have set up 2 here right so let us say this = LN so I am taking the natural logarithm of what do we say here I am going to assume C naught is going to be a constant so right it is CT is first this case this divided by 195 and bracket close and enter.

So what am I doing here I am just calculating natural logarithm of CT / C naught right so same case here I just give the same what do we say equation here for all the cells here so now obviously I need to calculate the model what do we say natural logarithm of C / C naught of that obviously I need to choose some value of K so I will start with let us say the value that we had earlier that is equal to 0.29 I guess right or 28 that is fine.

So let us go with = - K times T where is T into time here right and obviously I need to keep this cell constant with respect to the K and so I have to say control Z dollar symbol so I guess this helps me in keeping this cell constant again dollar symbol right so enter okay and I am going to use the same formula here.

So now I have that here right and again why did we have enter please okay and where we looking at – KT as we looked at it here right we know that what is it now natural logarithm of CT / CT naught = - KT right to be able to calculate model value of natural logarithm of CT / C naught and assuming some value of K and then calculating this model value of CT / CT naught right so that is the approach and that is what we have here and the I have trail and error and we say trail value of K here and so error obviously = the difference between these two values – enter.

So I am going to use the same here and then = this cell to the power of 2 right and now let us say this is equal to some of all these is enter and this some of squared errors. Say again now I am trying to be able to trying to calculate the rate constant that would give the least sum of squared errors right what would that mean that mean that the K value would be closer to the true value right.

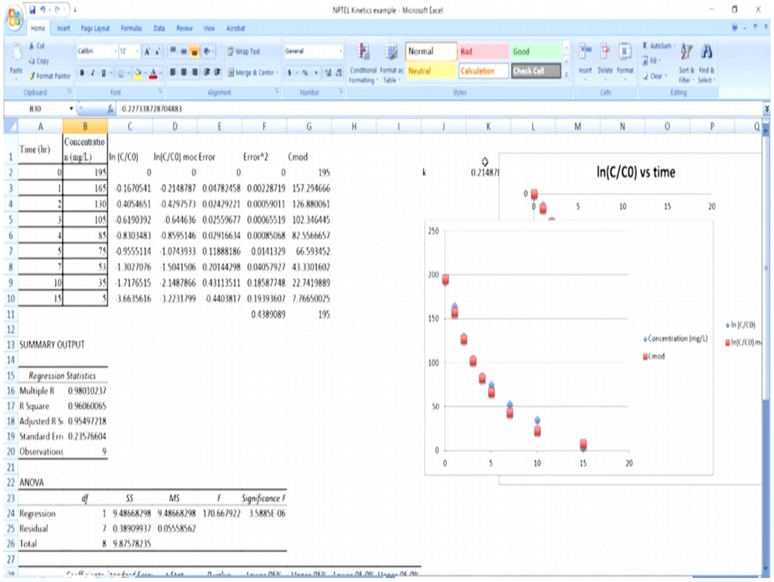
So let us try to approximate that again so back to solver right and then target serve is obviously to this error right and it has to be the minimum and by which cell I guess right I has to be K2 it seems to be set it K2 right okay and I am going to ask you to solve it right I have 11 and K2 okay solve and looks like I end with value of 0.21 and you see that the error has decreased I guess right and now you see that we started out with what do we say value of K to be around 0.29 but looks like model or the value that would best fit the given data would be your value of 0.21 I guess right.

So let us just write that down here before we move on right from linearized we have the value of K to be 0.21 right so now for non-linear approach I guess. Non-linear approach has not I am going to what do we say transform this equation for this I have CT = C naught into E power – KT right and let us say I am going to look at this particular case right and then what do we say without transformation just look at the relevant value of K come with CT model right.

And how do I calculate CT model here if I take some trial value of K I know CT and I am talking C naught in this case to be a constant which is good enough what do we say assumption or if you want to you can also assume that C naught is also variable let us say but in general the first variable that we have let us say is something let us say in which we have greater confidence let us say right.

So if you want to you can also have C naught has a variable or let us say in this case we are going to have C naught as a constant so from that let us say plugging in some trail value of K I know different values of T right I can calculate my CT model right and already have CT the concentration experimental value already given again I will calculate the error square and so on and so forth.

(Refer Slide Time: 52:16)



B30 -0.227338728704883

Time (hr)	Concentration (mg/L)	ln (C/C0)	ln(C/C0) moc	Error	Error^2	Cmod
0	195	0	0	0	0	195
1	165	-0.1670541	-0.2148787	0.04782458	0.00228719	157.294666
2	130	-0.4054651	-0.4297573	0.02429221	0.00059011	126.880061
3	105	-0.6190392	-0.644636	0.02559677	0.00065519	102.346445
4	85	-0.8303483	-0.8595146	0.02916634	0.00085068	82.5566657
5	75	-0.9555114	-1.0743933	0.11888186	0.0141329	66.593452
7	53	-1.3027076	-1.5041506	0.20144298	0.04057927	43.3301602
10	35	-1.7176515	-2.1487866	0.43113511	0.18587748	22.7419889
15	5	-3.6635616	-3.2231799	-0.4403817	0.19393607	7.76650025
					0.4389089	195

k 0.21487

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98010237
R Square	0.96060065
Adjusted R S	0.95497218
Standard Err	0.23576604
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	9.48668298	9.48668298	170.667922	3.5885E-06
Residual	7	0.38909937	0.05558562		
Total	8	9.87578235			

So let us move on so here I guess I set it up right so that is equal to C naught is 195 into capital EXP so exponential of – and I need to take some trail value of K so I guess I refer to this cell and I am going to change the letter into and time here bracket close and also heritage such that I am going to keep this cell constant dollar symbol here and again dollar symbol and K value again let us going to start with my trail to be around 0.29 right okay.

And then I am going to just copy this here so here we have the model of values this based on let us say what do we say this particular trial value of K right and then error is nothing but the difference of these two cells right = - this and enter and error = this to the power of 2 and now sum of squared errors = sum of all these cells right enter so again what do I need to do again I need to change the value of K so that I will get the minimum value of this sum of squared error right.

So again I need to go back to solver right and then let us look at the particular cell okay I need to change E 11 the minimum value I am looking for minimum how do I get that by changing I 3I I guess right okay looks like it set and I am going to solve for it okay keep solver solution and now looks like I have an error of for an error of 152 let us say the K value around 0.19 I guess right okay so now for this particular non-linearized what do we say regression I have a value of 0. I believe 19 right okay 19 0.19 I guess right.

So I guess depending on the approach you do have what do we say minor variation in the model value right that if you want to compare two models how would you do that I guess right you are going to look at some of the squared error right and choose that particular which would give you the lease sum of squared error for example here we have two rate constant so right 0.21 and 0.19 which one need to choose for that obviously you are going to look at let us say the model of that which will give you the least sum of squared errors.

So let us look at the sum of squared errors for this I believe C3 is corresponds to the non-linearize model I guess right so here K was 0.194 and sum squared errors 152 let us look at the other case. So here I guess K was 0.21 for the linearize model and for sum of squared error is 0.43 but we cannot compare the like for like because here the error corresponds to natural logarithm of C / C naught.

So let us just calculate the C mode for this particular K value CT = C naught in this case 195 right into exponential of –K times right and K this cell is constant I am able to set it accordingly right into T right and T is here and going to say that is the case and enter and copy that here right and now I need to calculate the error for this particular case I again calculating the error because I want to be have a like for like compassion of sum of square errors so in this non linearize model we had the case for CT and calculate the error accordingly.

So here too I am calculating CT of the C model I guess right so the error square I am going to calculate the error square ah directly let us say here right = C model one – the actual right to the power of 2 right and then if I drag drop and here is going to be sum of squared error right sum of squared error is and so if you see as error sum of squared error with this linearize model this for the linearize model right is 404 for value of rate constant of 0.21 I guess.

But as you see here for value of rate constant of 0.19 looks like the sum of squared error is lower which is 152 in this case and thus I guess the non-linearize regression actually gives us better or better for best fit moral I guess right. So here I guess I have a few graphs that I would like to look at so let us go back to sheet 1 right this is a particular case right let us try to understand what we have been up to.

So here I guess the blue what do we say data sets corresponds to the experimental values or the measure values right these two what we say data's sets and the rate or red dot let us say rate model corresponds to what we have let us say based on the values of K and N being what do we say 0.29 and being 0.9 right so again we can look at that right rate moral I guess right.

So again as you see now right what is this does solver helped us it helped us what do we say come up with a set of what do we say set of constants that would best approximate the experimental data which is the blue data point for example let us say if I change the value of K let us see how this data changes let us go with 0.35 okay and now you see that the moral values let us say or what do we say further aware from what do we say the experimental value let us increase K for that to 0.5 let us say.

So 0.5 again you see now further i guess there is what we say deviation from the experimental value which is the blue data and the red data set which is the model data set and again at the same time you see that the error as you know kept on increasing I guess right so let us go back to what was our value 0.28 I guess right 0.28 so now you see I guess the error is minimum right and also even graphically now or visually you can see that the moral data set and the experimental data set or what do we say inconsonant with each other.

Again to illustrate this let us say N and let us say 2 and now you see that you know the makes no sense the order I guess is now 2 rather than 1 so let us go with 1 right if which choose just N = 1 and K to be the same value of 0.29 you still see there considerable error right but you know that the order of value that theoretical value needs to be what do we say integer.

So thus we round it off N to 1 instead of choosing 0.9 and then we calculated the K value which should again see to that it is data set would what do we say or K value which could be the best fit and I think we did that in sheet 2 so here I have the data set right and let us say I am going to drag this here so here let us say we have natural logarithm of CT / C naught versus time right that is what I have here blue data set is the true data or the experimental data and red data I guess is the ahh moral data right and that is what you see here right.

Even here let us say change different values of K and C how it changes let us go with 0.29 right and you see that there is deviation from the data let us go with 0.1 right again you see deviation from the experimental value which is the blue value right. So the true value of K right would give you a data set or a moral which would see to it that error or the difference between or the some of squared errors when you look at it with respect to eh moral data and the experimental data is going to be minimum right.

So let us go back to I think another 0.21 okay now you see that this is minimum I guess right so the same time I also calculate CT and this is the graph right so now let us go back to non-linearized what do we say regression right and same case here so here instead of nation logarithm of CT / C naught we looked at C versus time again say we end up with 0.195 I guess right and for that again the graph we have the graph here between the moral value and the true value right.

Again visually too I judge that let us say it is a pretty good fit or how can you quantify that you can quantify that saying that you know the some of the squared error is less or the minimum so let us just try to 0.29 let us say 5.29 and you see that the moral value now does not approximate the true values will let us go with lesser value of 0.1 right and now again we see the further shift to the other side of this set of data right and here I have the relevant aspect I guess right.

Can I go back to the true value okay this is the true value and you would have observed that the true or the best it value I guess this some of squared error would be minimum right so if I also want to look at what do we say different aspect let us say what do we say excel have a few built in options let us say with respect to trend line say if you can go to that let us say choose either between linear or exponential model.

But obviously it has limited set of models and then it can calculate let us say what do we say based on again the same approach of regression the value of the relevant variables right but obviously again you know that is going to be slightly different from what would be true value but this is the approach for regression at model or built in model you use right again another approach would also go to say data analysis.

And let us say this will not work for non-linear let me look at linear approach and you know demonstrates some other aspect so I am going to go to data and data analysis and let us say I need to go to regression okay and regression so input Y range I think we were trying to look at what is it now natural logarithm of CT/ CT naught and what is it now the time I guess right and here I can input the relevant values let us say and then calculate again based on regression the relevant aspects here again right.

So let us try to get that done I guess right so input Y will be at CT / C naught right so Y range I guess was the concentration so I am going to say Y data set right and okay it should have them natural logarithm of C/ C naught delete please so we are looking at the linearized version here right.

And so obviously I need to give the linear data or linearized data natural logarithm of C / C naught and X range was I guess what is the X range it should have been – K times T so I need to calculate that before I go further right or I can give T though that should also worth right and working so output range I am going to ask the data to be given somewhere here working and also want to have let us say residuals I guess right and residual line plots that is fine.

And so here again this is a building tool but usually work only what do we say for linearize form for that I am going to look at demonstrating how to get that done. So here I guess I have the output right and let us look at the values here right so incept I guess I come out to be what is it now 0.11 and X variables which is your what do we say rate constant is around your 0.22 right.

So here again you see that the rate constant right again approach this the value that we calculate here which was around 0.214 right and that is what you see here right. So again in the form of Y = MX + C right we see that M = slope here and if you look at the natural logarithm of CT / C naught = - KT right and in that I guess KT is nothing but your slope here and that is slope which is the X variable which is – 0.22 but you know it is KT model now the K is 0.22 right.

But here the moral consider the intercept that is why the X variable was different from what we calculated by us what do we say fundamental approach. So in your particular data analysis or regression when you went there or when you went to that or we went through that if I said that incept to be 0 I would have got in the true value to be closer to the value of 0.21 I guess so different approaches but this suppose that we looked at is the fundamental value I guess right.

So i guess with that we have done with the aspects related to kinetics right and now I guess from the next session we are going to move on to acid and basis right again kinetics give us an idea about how fast let us say system or a process what do we say goes through I guess right and in that context today what did we look at let us say in the second part of the session let us say we looked at let us say how to fit particular data let us say pardon me not a data a model to a particular set of data and get the relevant constant so that they approach the true values.

And for that what approach have we looked we looked at regression I guess right so I have set of data I want to calculate the relevant variables for the best fit how do that by minimizing the sum of paid errors I guess right so I guess with that I will be done for today and thank you