

welcome to this next class on chemical kinetics so before ah you know i start with the proceedings of today's class i'll you know as usual i will do a brief recap of what we did in the last class and this is what if you would remember we were talking about the kinetic analysis of experimental data and one of the things we started with was the average rate so the average rate as you can see out here is defined by the concentration difference over defined time difference or interval which is  $\Delta c$  over  $\Delta t$  and if it is obviously reaction then this average rate is always preceded or this gradient is preceded by a minus sign okay now apart from this average rate what we also have is something known as instantaneous rate so this was the next one which we were discussing and what is the instantaneous rate the instantaneous rate as defined by the what instantaneous means that we are trying to figure out the rate at any given instant right for example whether it is  $t_1$   $t_2$   $t_3$  and so on if you you know if you see these remember these dots or green dots if these are your you know respective times then what you would do is to get the instantaneous rate you would draw a tangent at that point itself see for example if you would you know if you would try to get the instantaneous rate out here right which is defined as  $t_1$  then you would draw a tangent at  $t_1$  and what will happen is then this  $r_{\text{instantaneous}}$  the rate which is instantaneous rate is equal to the negative of the  $d$  of  $r$  over  $d$  of  $t$  where  $r$  is your reactant and in brackets it means the concentration of the reactant ok so ah the instantaneous rate is also a very important feature its one which is mostly used and ah as i was saying ah just now the instantaneous rate is achieved by or obtained by drawing a tangent at that instant or at that time point which is  $t_1$  and from there we take the slope of the tangent so for products what would happen for products exactly the same thing only that the products appear as a function of time so  $r_{\text{instantaneous}}$  which is this would be equal to  $d p$  over  $d$  of  $t$   $p$  being the product appreciated by a positive sign because the product is appearing as a function of time ok then we move down to the initial rate of the reaction so initial rate again as the name suggests is at the very beginning of this reaction at the very start of the reaction ok which is very close to time zero you know time zone is very

much at the initial point of the reaction ok  
so you can see from here the initial rate can  
be obtained from the slope of the tangent at that point similarly we can do  
the same thing for  
product again at time zero you see the product is gaining as a function of  
time that means its  
coming into being into existence as a function of time and what we are doing  
is we are getting  
the initial rate by drawing a tangent at the very early time point for the  
product a couple of other  
points we also mentioned about this initial rate it is preferable to do the  
initial rate  
calculation based on a product appearance as it is mentioned out here and  
this is because  
you know remember when you have no product to start with and you have  
reactants to start with  
and you know suppose suppose your reactants are colored your products are also  
colored having  
a different color okay now if ah you are if you are ah trying to get this  
initial rate by looking  
at the change in concentration of the reactant then what would happen is  
because it is the  
initial rate the change would be  
so small that you might not detect much but however think about  
the product if there was no product to start with right but the moment some  
product appears you  
know you see a visible change out there because there was not no product as  
such and suddenly some  
product came into existence and hence looking at the product is always a  
better option if you are  
going to calculate the initial rate i hope i have you know made myself clear  
with regards to that  
then ah the initial rate calculation as the second point says has to be done  
very close to  
the starting point that is ah often within five percent of the start of the  
reaction ok  
so except  
chain reactions you know chain reactions are quite complicated the initial  
rate line or the tangent  
will always be the steepest one that means the one having the maximum slope  
and it makes sense  
because at the initial point your rate of reaction is also the maximum and  
hence the slope or of  
the line is the steepest ok  
so the last thing we were discussing that day was this you know  
dependence of reaction rate and concentration from here what we plan to do as  
you would see is  
go on to rate expressions  
so lets you know focus on this again for some time  
so what we said was  
that you know this is a typical reaction profile where we see the  
consideration of reactant  $r$  being  
given on the  $y$  axis and the time being given on the  $x$  axis and obviously the  $r$   
being the reactant

its concentration is you know decreasing as a function of time if you follow the blue line now

what happens is if you take you know definite time points like say this  $t_1$  you know  $t_2$   $t_3$

and  $t_4$  and try to calculate the instantaneous rates at all these at all these essentially the

slopes what you will see is that the slope of this tangent a b is greater than the slope of

this tangent c d is greater than the slope of this tangent e f is greater than the slope of the

standard g h

so as it says if the instantaneous rate is equal to the slope of the tangent and with

you know a negative sign negative referring to the loss of reactant then what we see is that

a b is having the maximum slope followed by c d followed by e f followed by g h which is having

the minimum slope again g h being this a being this a b is having the maximum slope g h is having

the minimum slope and then in between we have c d and e f again just to remind you of our previous

discussions on slopes that when i am referring to the maximum and minimum slopes what i actually

mean is the respective magnitude of those slopes ok

so please always keep that in mind

so then what does this tell you it tells you something what it tells you is that maybe the reaction not maybe the rate of the reaction is proportional to the reactant so

let us you know try to ah put that in words

so lets talk about this

so from this you know from

this graph what we can conclude is the following that the rate of

so i'll just change

the pen reaction the rate of reaction is in some way dependent on the concentration of the reactant again the rate of reaction in some

way is depend upon the concentration of the reactant why do we say that again lets go

back to this figure see at time  $t_1$  i have a certain concentration of the reactant r at time

$t_2$  i have a certain concentration the reactant r at time  $t_3$  have certain constant of the

reactant r and

so on and as i increase my time what is happening is that the concentration of

the reactant is decreasing now not only that based on the slopes that have you know the

tangents that we have drawn out here you can see that along with the decrease of the reactant along

with the decrease of the reactant concentration the slope is also decreasing right the slope of

the tangent is also decreasing

so for example at time  $t_1$  whether you know amongst all these time

points  $t_1$  or  $t_4$  at time  $t_1$  where the concentration of the reactant

is the highest the slope is also the highest then i go to the next one where the concentration has decreased a bit at time  $t_2$  then the slope has also decreased i go to the last point  $t_4$  where the concentration of reactant is the lowest then the slope is accordingly also the lowest hence what we can write is

so the rate of reaction is in some way dependent upon the concentration of the reactant then i add this word remaining remaining means whatever reactant is remaining after some of the reactant has gotten converted into product

so i can write that the rate is equal to or say let me write this not equal to let me write this as a proportional sign proportional to the concentration of reactant to the power  $n$  right

so let this be equation one now this is significant what you are saying is based on the you know graph or the plot you just saw the kinetic profile you just saw based on this what we are concluding is that the rate of the reaction is depend upon the concentration of the reactant that is remaining and based on that what we are saying is then that the rate of reaction is proportional to the reactant raised to some power which in this case is  $n$

so what is  $n$  so  $n$  so what is  $n$  so  $n$  is a number which states exactly how the rate depends on the reactant concentration right so this is important it states exactly so this  $n$  states exactly the nature of dependence of the reaction rate on the concentration of the reactant  $n$  therefore is the order of the reaction right  $n$  is the order of the reaction and we can go ahead and write we can remove the proportionality and write that

rate is equal to  $k$  times the concentration of reactant raise to the power  $n$  let this be equation two ok

so obviously now you realize that this  $k$  is my constant of proportionality my constant of proportionality and hence this one is called the rate constant ok again this is a very important term and chemical kinetics which is the rate constant

so what is then read equal to rate is equal to the rate constant  $k$  times the concentration of the reactant raised to the power  $n$  which is the order which tells us exact nature of the variation of the reaction rate as a function of the concentration of the reactant ok

so what does this equation tell us what it tells us is this that if  $n$  is equal to 1 then it is a first order reaction ok if  $n$  is equal to two right then we call its a second order reaction if  $n$  is equal to three likewise it is a third order reaction if  $n$  is equal to

zero refer to as a zero order reaction if  $n$  is three by two or three halves then you see it is a order which is fractional that means fractional order of three halves

so which means that if it if  $n$  is equal to one it tells that the rate is equal to  $k$   $k$  times reactant raised to the power one then if  $n$  is equal to two it tells us that rate is equal to  $k$  times reactant raised to the power two ok if  $n$  is equal to three it is a third order reaction  $k$  times reactant raised to the power three if  $n$  is equal to zero then this value of  $n$  is zero so which is called a zero order reaction order values that means  $n$  values can be fractional and this is what you see is

$n$  equal to three by two then i put three by two out here but in a nutshell what this is telling me is how the rate is varying or how the rate depends upon the reactant concentration now that's the most important part now suppose i have a reaction including two reactants that are  $a$  and  $b$  ok and what i found out was by doing an experiment this you know the you know the ways we try to find out the orders we will discuss those a little bit later after going to the integrated weight loss and all but suppose we do an experiment or sets of experiments to find out the rate or order of this and we say that the rate is equal to  $k$  into concentration of  $a$  into consideration of  $b$  ok and i would say that this would be let's see reaction ok equation number three if i put in now the way i read this rate equation is i say that this reaction is first order first order with respect to  $a$  or you know also i mean first or respect to  $a$  also it is first order with respect to  $b$  because you see rate is equal to  $k$  the rate constant times  $a$  raised to the power 1  $b$  raised to the power 1 isn't it right hence i say that it is first order with respect to  $a$  and the rate is first order with respect to  $b$

so if you take  $a$  if you take  $a$  then how the rate will vary it will vary as being first order with respect to  $a$  if you take  $b$  then how will the rate vary the rate will vary as first or the respect to the consideration of  $b$  then what we can say is that the total order the total order of the reaction is one plus one equal to two so what does it mean that the total of the reaction is the sum of the exponents where the exponent for  $a$  is one because first with respect to  $a$  experiment of  $b$  is one first with respect to  $b$  but the total order so as i say the total order here of the reaction then is one plus one which is equal to 2 ok please remember this this is also very important its being you know being a second

order reaction the order the way this equation has been written the order is because this expression has been written the order is equal to the sum of the exponents of the orders of the two reactants there is one for a and the x one for b being one so one plus one is equal to two if you take another example say where rate is equal to  $k a^b$  this before so what are you saying here so here experiments or by doing experiments we have found out that the rate for a certain reaction is equal to  $k$  times the concentration of a raised to the power two and consideration of b raised to the power one so we again say that it is second order right with respect to a first order with respect to b right and as before the total order the total order is equal to two plus one is equal to three right like before so the total out of the reaction is what the sum of the orders of the individual reactants that is exactly what you see out here that was what happened in the example before where it was rate is equal to  $k$  times concentration of a times concentration of b and what is happening out here is it is here the rate is equal to  $k$  times concentration a to the power raised to the bar two times the concentration of b hence the total order is two plus one equal to three ok so then these equations in the equations we have written out here so for example the equation you saw out here and the equation we wrote out here so if you can write the equations in a very general way say rate is equal to  $k$  right times reactant raise to the power say  $n$  or we can write rate is equal to  $k$  times reactant 1 raised to the power say  $\alpha$  then reactant two wrestle power  $\beta$  ok so its going out of the margin so in this case we see the rate is equal to  $k$  times reactant raised to the power  $n$  one single reactant raised to the power  $n$  the order in the second case we see rate is equal to  $k$  times reactant one raised to the power  $\alpha$  reactant two raised to the power  $\beta$  that means there are two reactants so these sorts i mean if i can say this is you know this is this is equation five you can say that this is equation five and this is equation six then we can say that these are referred to as rate expressions ok these are referred to as rate expressions or rate equations ok either rate expressions or rate equations right and what are they telling you what are they telling you is how the individual reaction is depending upon the component species if it is one species rest of the power  $n$  if there are two species say then one of the species raises the power  $\alpha$  one of the the second species of power  $\beta$

these being the individual orders of the specific reactions what we can now generalize saying that if I have a very general equation of the type  $a^{\alpha} + b^{\beta} + c^{\gamma}$  going to  $p + q$  and on if I have equations like this then what I can do is I can say that the rate expression or rate equation is equal to  $k$  the rate constant times concentration of  $a$  raised to the power  $\alpha$  concentration of  $b$  raised to the power  $\beta$  concentration of  $c$  raised to the power  $\gamma$  and so on and so on so if this is my rate expression right so if this is my rate expression say let this be equation seven if this is my rate expression equation 7 then the total order the total order of this equation is equal to  $\alpha + \beta + \gamma$  plus the rest of the exponents ok that is your total order and  $k$  is referred to as the experimental rate constant so order is an external quantity so is the rate constant here and having a very general having written a very general equation like this where  $a^{\alpha} + b^{\beta}$  the small letters being the coefficients so the big letters signifying the reactants and the products if the red expression is given like this right where the exponents show the nature of dependencies of the individual reactants for the rate then the total order is given as a sum of the exponents which is  $\alpha + \beta + \gamma$  and  $k$  being the experimental rate constant so again before I move forward this is a very general form of this red expression and being general form it typically holds throughout now there are some key points you have to remember the key points are like this what are some of the key points of the red expression you just saw so there is one concentration term for each reactant one concentration term for each reactant see for example where we had the reactants  $a + b + c$  right there was one concentration term for  $a$   $a$  being a reactant there was one concentration term for  $b$  there was one concentration term for  $c$  and so on then each concentration term is raised to a particular power right as you saw  $\alpha$   $\beta$  you know  $\gamma$  and so on so as again each concentration term say  $a$  was raised to the power  $\alpha$   $b$  was raised to the power  $\beta$   $c$  was raised to the power  $\gamma$  if I do a kinetic analysis if I do a kinetic analysis what would I aim to do here again I am doing a kinetic analysis what do you mean by that if I am doing this analysis what I

am

trying to get is i am trying to find the value of alpha beta gamma and

so on right

because i am doing an analysis by doing this analysis i am trying to find out what these respective exponents are alpha beta gamma and also by doing this analysis

i am finding the value of k which is the rate constant the k which is a rate constant at a certain temperature at a certain temperature

so when you

are doing a kinetic analysis what we mean by that is of any reaction what i mean is that

i need to figure out the respective orders for each and every individual reactant

involved and once i have done that i also need to figure out the rate constant k at a particular

temperature because remember rate constant is a constant but it does depend upon temperature

right and hence whenever we are trying to do this analysis we have to make sure that we do it

at a certain constant temperature because the rate constant is defined only for that

temperature the moment the temperature changes the rate constant value will change

because it has a temperature dependence a feature a very important feature of chemical kinetics which we will discuss later okay

so this was ah you know whatever we have

done up till now you know starting from the average rates instantaneous rates and

so on

so from there you see we have slowly moved on we looked at this ah you know we looked

at this initial rate after that we looked at how the slopes would differ at each and every time

point and from there we got an idea that the rate might be depending upon the concentration of the

reactant remaining ok after having done that we started working on the red expressions how the

rate expressions should be written what should be included in the rate expressions

so now the

rate expression we know it has the rate constant it has the individual concentrations if there is

only one reactant species then there is only one concentration if there are many reactant species

then there will be many concentrations like a b c but each of these each of these would have to be

raised to a certain power or they should be having certain exponents these exponents are referred to

as the orders of the reaction with respect to each and every individual reactant if there is only

one reactant say that is rate is equal to k times a to the power n that n is the order

of the reaction if there are more than one reactants there is multiple reactants

where we just saw rate is equal to  $k$  times  $a$  to the power  $\alpha$   $b$  to the power  $\beta$   $c$  to

the power  $\gamma$  and

so on then the total order of the reaction is  $\alpha + \beta + \gamma$  and like that ok

so these are some basic fundamentals which have to be absolutely clear before you

go ahead and start working with the concepts of chemical kinetics right having you know

done all these i will ah shortly look at the units of rate we know that what is rate rate

is essentially the change of concentration with time

so i can see the unit would be concentration over time

so if that's what it is the units are so

if your concentration is expressed in moles per liter there is a molar concentration

so you know time can be anything tank can be second time can be minutes and

so on see for example if concentration is in molar units or moles per liter then

what would the unit be the unit of rate is over time or  $m$  time inverse or we can write moles you

know over time or mole liter inverse time inverse remember time can be anything tech

can be seconds i can be minutes that can be hours depending upon the type of reaction you are

studying or looking at

so this is you know how the units would be written if ah the concentration would be expressed in molar units however for cases reactions for gaseous reactions one

of the common ways of expressing this is in atmospheres over time or i can write

atmosphere time inverse ok

so now if i say that if time is in seconds

so if time is being

expressed in second say then what i can write is for the molar unit you know for the molar unit

where the concentration moles i can write mole second inverse or mole liter inverse

second inverse and for gaseous i can write atmosphere second inverse right

so that is why this is very straight forward why because you know that the rate is how the concentration is changing over time

so that is what you have just done if your

concentration is in molar units you put in molar units moles per liter if your consideration is

in you know atmospheres for gaseous reactions you put in atmospheres and so on now lets

ah look at the meaning of rate expression

so meaning of rate expression now

this is again very straight forward it is the extension of the discussion we just had

so say for example the first one if rate is equal to  $k$  times

say you know the reactant  $a$   $k$  is equal to  $k$  times reactant  $a$  so

we obviously know then that this is a first order reaction ok there is a first order reaction which means that if you know concentration of a is increased if concentration of a is increased by a factor of two say if the concentration of a is increased by a factor of two then the rate also increases by a factor of two straight forward right rate is equal to  $k$  times  $a$

so increase consideration  $a$  two times there it also increases two times similarly if consideration of  $a$  is increased by  $ah$  so this by a factor of six say that means the concentration of  $a$  has been increased six times then rate is also increased by the factor of six ok

so when consideration of  $a$  was increased two times weight was increased two times when the consideration of  $a$  was increased six times rate was increased six times this is the concept behind the first order reaction however if we take this case where the rate is equal to  $k$  times you know the reactant  $a$  raised to the bar two

so obviously we done we say there is a second order reaction when we say its a second order what do you mean we mean if concentration of  $a$  is increased by a factor of true two then rate is increased by a factor of two raised to the power two which is

four difference you see first order it would be two if its two this is power one second

order it is two raised to the power two similarly if concentration of  $a$  is increased by a factor of 6 by a factor of six then rate is increased by a factor of remember it is increased by a factor of six right

so now its six you raised it but then to the power two which is again you see the difference if this was a first order reaction the rate would be increased by a factor of 6 to the power 1 which is 6 it is this being a second order reaction the rate is not increased by 6 to the power order which is two there is thirty six ok

so these ah you know are some things we should be able to tell right away when you look at the rate expression then if you have rate is equal to  $k$

times consideration of  $a$  to the power zero remember now  $n$  is equal to zero which means it is called a zero order reaction that means the rate is zero order with respect to the concentration of the reactant which is a

so which means no matter no matter what the concentration is no matter what the consideration is of  $a$  the rate will remain constant right

so this being a zero order reaction  $k$  raised to the power zero it means that the rate has no dependence whatsoever on the concentration of the reactant you have taken

so you can vary the concentration of the reactant many fold many times but the rate is absolutely not dependent on the concentration of  $a$

so like you know we did you worked out the units of the rate we can also work out the

units of rate constant again this is very simple right this is very simple we need to know the rate expression say for example i do a first order reaction ok i do a first order reaction ok and in this first order reaction we know that the rate is equal to  $k$  times concentration of  $A$  right very simple so because it is the unit of rate constant i am looking at right remember it is unit of rate constant i am looking at right now not the rate but the rate constant so what is  $k$  then  $k$  is equal to the units the consideration of  $A$  over the unit of rate right now the concentration of  $A$  is say expressed in molar concentrations or moles per liter moles per liter that is a consideration of  $A$  we know that the consideration of  $A$  as  $r_A$  the unit of rate we just derived before it is what sorry i ah you know ah extremely sorry i just had it reversed so ah just hold on so let me take ah let me actually ah cut this hold on so this is so this remains the same i wrote this one ah wrongly so what i should write is extremely sorry so  $k$  is equal to  $\frac{r_A}{[A]}$  ok extremely sorry for that so rate is equal to  $k$  is equal to rate over consideration of  $A$  and the concentration we knew say is small liter inverse and then what we are doing is we are putting the unit of rate out here so we go to the next page we write it a little ah in a better way because i have done some cancellation so  $k$  is rate over consideration of  $A$  the constellation of  $A$  is mole over liter so moles per liter or molar concentration now remember rate was consideration over time so i will be writing moles liter then time inverse ok and hence the unit of  $k$  will be that of time inverse right because this moles per liter demonstrator cancels from the numerator and the denominator so the unit of  $k$  is time inverse so if  $t$  is second so it can be second inverse you know it can be minute inverse it can be hour inverse  $h$  standing for hour hour inverse and so on right so hence for a first order reaction of the type rate is equal to  $k$  times  $A$  for a first order reaction rate is equal to  $k$  times  $A$  the unit is the inverse of time ok so likewise we go to ah in the second order reaction so here let us take this example where rate is equal to  $k$  times concentration

of

a raised to the bar two two being the order in this case two hence second order

so therefore k is equal to rate over a squared okay rate over consideration of a squared ok

so again what was rate moles liter inverse consideration being expressed in molar units or moles per liter then time inverse over over what do we have we have the concentration of a raised to the power 2 hence we would be having moles liter inverse raised to the power two ok and thus we will

be having as

so one of these would cancel out right

so this will go on top

so i

will be having mole inverse liter time inverse and the better way of writing this a better way of writing this is

so you understand right this is moles per liter one of the moles per liter is cancelled out you are left with one more moles per liter that goes

on top

so if it becomes moles mole inverse liter time inverse now the general way of writing this

is let see this ah liter is having the positive exponent

so you always bring the positive exponent first

so you write liter mole inverse time inverse ok

so this then is the unit of the rate

constant for a second order reaction again the time can be anything you can replace it

by second you can replace it by r you can replace it by minutes depending again upon the reaction

you have enhanced and as i ah told you again this the way it is written is this you just make

sure this is not wrong but what you just make sure is that a better way of expressing this is that

the one which is having the positive exponent is written first

so i have taken later

first x raised to the power plus one and negative exponents are written later ok

so carrying on with the same ah concept if i you know go for say a zero order reaction say now if i go for a zero order reaction as we have seen before rate is equal to

k a raised to the power zero right now because it is raised to the zero anything raised to the

power zero is equal to one hence i can write rate is equal to k

so what does it mean

that means the unit of rate constant is equal or is that of the unit of rate means rate is equal to k

so then the unit of k is equal to moles liter inverse time inverse ok again please take care of one thing here you

see the mole is having the positive exponent so i have written this in first and then the later

inverse and the time inverse they come in later ok

so with respect to you know the units of the

rate constant

so this is how you always figure out see there is not this is you know this is not something that you have to memorize once you have the red expression in front of

you you know what the unit of rate is always concentration over time you know the ah you know

the units of your concentration for the reactants and given the rate expression you can always

do this and find out the corresponding unit for the rate constant so there is minimum

memorization maximum concept or understanding

so let us you know do a quick example ok what does this example say

so the

example says that ah there is a reaction where

so i have a reaction say well let this be a

so i have a reaction which is first order with respect to a and first order with respect to b and the reaction the reaction is happening between a and b ok

so now what you are being

asked is now what you are being asked is give the rate expression

for this and you can assume time to be expressed in minutes ok

so you said

that there is a reaction between a and b the reaction is first order respect to

a first with respect to b and the time which you should take the unit of time is minutes ok

so this will be the last thing i am going to discuss in this class today

so then based on our previous ah discussions i can write the rate of the reaction is equal to k

times concentration of a raised to the power one times consideration of b raised to the power

one both being first order

so you can write a b this is the rate ok

so the moment i have

written this i can though it was not asked then the overall order or the total order

is one plus one equal to two right and then because this is what in a second order

reaction then you know what can i write i can write is that the unit

of k the unit of k is equal to rate over consideration of a

consideration of b i know that the rate is moles liter inverse and because the time was minutes minute inverse and then i have the consideration of a

expression moles or molar concentration and this one also in molar concentration is moles per liter

so the moment i do this i

can see i get this is equal to liter mole inverse minute inverse this was an example where we have been told

that the reaction is first with respect to a first with respect to b write their expression

the total order is one plus one equal to two once you write in the total order now this

was simple because you had done this before we had done this before in the sense that

we had taken rate is equal to k times a raised to the bar two but here we have taken two

different reactants each raised to the power one but total order is two and hence you get again the same value of the unit for the rate constant okay we will stop here and we will carry on ah from ah this you know place in the next class thanks you

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