so let's start with today's class just where
we left off uh yesterday remember we were talking about
so this was lecture number seven
and yesterday the last part of lecture number six we were talking about the units of rate constant
right and you know for a first order reaction we found that the unit of rate constant would be the
inverse of time that is either inverse of second minutes hours right if you go for a second
order reaction
so it would be like this litter mole inverse time inverse making sure
that whichever is having the positive exponent is written at the very first and then ah you go
to a zero order reaction
so for the zero order reaction what happens is the rate is equal to
k times ah the concentration of the reactant raised to the bus zero that means rate is equal
to k
so whatever the unit of rate is that turns out to be the unit of k the rate constant we
did a very quick example and the example was that if you are given a reaction where both
a and b are involved as the reactants and it is told to you that the reaction is first order
with respect to a and first order with respect to b then can you write the rate expression
you assume the time to be in minutes ok
so this was the last thing we did
yesterday where we saw that if we have this as given according to the question rate
is equal to k times a raised to the power one concentration of a raised to the power one
concentration of b raised to the power one then the overall order is one plus one equal to two and
then what is the unit of rate constant the unit derivative constant then turns out to be the unit
of rate over the unit of the concentration of a times unit of the concentration of b and hence
this is what we end up with now quickly if you do ah you know if we ah do you know one more
thing which is suppose we take another example rights continuation of the same thing we say this
is example b ok we have a reaction ok between a and b ok
so these are the two reactants
and it is again said that the reaction is first order with respect to a and ok say second order with respect to b ok
so then when you write
the rate expression
so the rate expression obviously becomes like this is
equal to k which is rate constant times concentration of a raised to the
power one because it is first order consideration of b raised to the power
two because it is second order hence k a b plus bar two and then based on
this i can write that the overall order of the reaction is one plus two equal to

three
 so now having you know discussed about these   it should be straight forward to you why it is one
plus two equal to three this being the overall or   total order of the reaction ok now what
about the units of rate constant
 so the   units are rate constant would be then
k equal to rate over concentration of b squared right
 so i can write you know what rate
is
 so rate is concentration over time here the   time again you assume the time to be in minutes
so it would be mole liter inverse mini inverse and then i will be having i can say mole liter there is a unit of consideration
of a and in this case i will be having mole   later raised to the bar two why because
it is second order right
 so here now   as you will ah realize that the first mole liter
and this one cancels out and i will be left with   liter squared mole to minute minus one
 so then this would be the unit of
the rate constant k okay and again   what you should pay attention to is that i have
written letter raised to the power 2 as the first   term why because here i have the positive
exponent and then the negative ones come later   you know hopefully now you can ah given a
certain rate expression or given a question   like this you would be able to find out the
rate expression write the rate expression   find the total order of the reaction and then even
go ahead and find the units of the rate constant   having looked at rate expression and
also having looked at the rate constant   you must be wondering about
this what is the significance of rate and rate constant well what i mean by this will ah soon
be clear you know when i go ahead with   this topic now what happens is because rate
depends upon the concentrations
 so rate   will vary with the concentrations of your reactants ok
 so the rate will vary with the concentration
of reactants then what it becomes is a problem   when if you are trying to compare you know reactions why   because if you change the concentration the rate will change right
 so what i can say is this the rate is not of much use
again the rate is not of much use in quantifying in quantifying reactions or comparing reactions right
 so this is important
because it says the rate is not of much use   well it it makes sense right because the moment
you change the concentration the rate will change   comparing reactions you know the concentrations if
they differ then again you cannot compare the rate   however there is way out what is the way

out well the way out is you realize now what i am trying to tell you or what i am
trying to ah reach at is that the rate constant is a constant at a given
temperature right and is independent independent of the concentrations
concentrations of the reactants ok there are few important terms out here
so the rate constant is a constant at a given temperature this is important because
rate constant does depend upon temperature you know the ordinances equation which will
come to later and also it is independent of the concentrations of the reactants
right hence you can see as opposed to rate can easily be used that means the rate constant
can easily be used to sorry to quantify and compare reactions ok
so while rate of the reaction is in some sense useless because it depends
on the concentrations but the rate constant at any given temperature is independent of the
concentration of the reactants and hence you can always use to quantify or compare certain
reactions or compare reactions not only that if you know the rate constant and
the order of the reaction you can easily write down the rate expression right
you can easily write down the
rate expression for that reaction ok
so because you know what is rate is equal to
say k times concentration of a raised to the power n like we had done before say rate is equal
to k times concentration of a the reactant raised to the power n which is the order
so if
you know the rate constant k if you know n then you easily write down the rate expression
so that
was in some sense the significance of the rate and the rate constant ok you can understand the
rate constant is fundamentally much more useful because of the fact that it is a constant
independent of the concentrations but do keep in mind it does depend upon temperature so
if you are comparing two different reactions you better compare them at the same temperature
because rate constant would otherwise differ whatever we have done up till now in you
know when we are talking about the rates you know the average rate the instantaneous rate and
all these things we were mostly focusing on what drawing of tangents right but the drawing of
tangents ah is you know not always advised right
so for this what we do is
we go for something known as integrated rate loss integrated weight loss or
integrate rate or i can write rate equations ok integrated
rate equations or rate expressions whatever
so i was telling you this up
till now what we did was to find say suppose i would like the instantaneous

rate ok
so suppose i am given a kinetic profile like this ok
so this is the concentration of a versus
time t and someone would tell me ok fine ask   me find the instantaneous rate somewhere here
what i would do is i would actually then draw a tangent and then try to find out the instantaneous
rate but then the problem is that how accurately   you draw the tangent will determine how
accurately you figure out the instantaneous rate that is why this is not the preferred way of doing
it all the time however however keep this in mind   that if you are going to have you know   complex reactions which means the reaction is not
straight forward or there are secondary reactions   you know you know it makes ah the whole
reaction scheme very complicated then obviously   the way you would figure out say the instantaneous
rate by drawing a tangent or the initial rate   by drawing a tangent at the initial point
would still be the more favorable ah way of   calculating the rate of the reaction
but however for reactions which   are relatively straight forward we would rather not use the tangent expression or   you know the ah the method of drawing the tangent
and then figuring out the rate instead we would   do something which is related to this title
the integrated weight loss or the integrated   rate equations ok now this is ah you know one of
the main aspects of chemical kinetics from where   based on the integer weight loss you can
do a lot of manipulations lot of things   but before i go to indicate weight loss i would
like to bring to your notice a very important aspect or a very important parameter in
chemical kinetics its called half life for a given reaction now why was   this concept necessary and why or in what sense
is it useful now again suppose you are given a kinetic profile like this where this is the
concentration of the reactant and this is the time   okay now yes one thing is that i can go and derive
the indicated rate expression and work based on   that but if i want to take a step back and based
on this kinetic profile i want to say something   at the preliminary level about this reaction can
i do that and if i can what would i base it on   what is that value what is that term what is
the parameter that i would base my initial value or my initial you know focus initial
explanation which would lead me to some deeper   insights about this corresponding reaction without
having to go to the integrated rate expressions
so that is why this half life
was some sort of a preliminary check based on the kinetic profile
so that means based on

this kinetic profile as you see can we say something about the type of the reaction
that you have or your study ok
so then this importance of half life was first coined by wilhelm ostwald he was awarded the nobel prize in nineteen o nine he was at the
nobel prize in nineteen o nine and he was earn an old prize mostly for his work on catalysis and also for ah providing many of the fundamentals of chemical
equilibrium and chemical reactions kinetics
so willem oswalt
so this would be l
sorry wilhelm osfald was the first person who said that half life at the preliminary level
would already tell us or provide us appreciable or significant information about the reaction
that we have in our hands or that we are studying
so let us go and try to see what this concept
of half life is
so when we say you know when we say half life what we mean by that is that or we
are trying to define half life right
so half life this is the time
so remember its half life half life is defined
in terms of the time
so this is the time it takes it takes for the concentration the concentration of the reactant
so again what is half life half life is the time it takes
for the concentration of the reactant to fall to one half one half of its initial value
so again what is half life half life is the time it takes for the concentration of
the reactant to fall to one half of its initial value now this is important ok how
do we visualize this on the graph itself or the kinetic profile itself again as usual let us draw a kinetic profile ok
so as we always say this is the concentration of the reactant
the reaction being a and this is time whatever unit it be seconds
minutes hours now suppose we have a profile which goes something like this ok
so this is my reaction profile or kinetic profile for a certain
reaction ok now this value
so this would be time 0 for me exactly the initial time
so this value
out here is my
so i can write here this is a zero
so what is a zero
so then a zero is the initial value of the reactant
so that means at the
moment the reaction is starting the value of this reactant is a zero
as zero refers to time zero then by the definition of half life if you
remember by the definition of half life the half life would be the time it takes for the
concentration of the reactant to fall to one half of its initial value
so if this is zero this
is a naught somewhere here then this comes to half a naught right its not

exactly drawn to
scale but when it comes to half a naught is half a naught this time from here to here is
called t half well i will come back to this again   now what you can also figure from here is that
if i have having half a naught
so from here to   here i can again come to half of it
so let
this be
so let this be ah
so let me put this ok
so then this is one fourth a naught right and i can even go and say that ok this is half of this gap
and i can write one eighth a naught ok
so just let me
complete this then i will explain what i am trying to achieve out here right ok
now lets look at this
so let this
so let this be corresponding intervals time intervals and remember i have my time access on
the x axis the time on my x axis right so
so now look from a naught the half life
says that is the time required to go down   to half of the concentration of a naught
which is half a naught
so this would be my t half i can say one i will tell you why i am
saying one now again when i reach half a naught
so then between zero and half a naught i can
again again decrease the concentration by half   which will become one for a naught
so this
one for a naught would be my next time right
so from here to here
so for example from here
to here you can see i can write this is t half two right and again this would be t half three
ok
so which i did not mention before
so this   t half is referred to as the half life thats
the symbol of half life that we always use right   when i go from a naught to half a
naught the time it takes me to go half   to go to half of my initial concentration is
t half right now we see here in red i have   written t half one t of one means again if
i write here t of one means the first half life then whatever t half two
t of t is the second half life   what is the second half life second of life is
the time it takes my concentration to fall from   half a naught to half of half a naught which
is one fourth a naught
so then t half two is my second half life and likewise t half three is my third
half life right the concept of half life is the   same what is it it tells you at the time it takes

for me to go to half of the initial concentration   of the reactant right
 so if my if my initial
constant reaction is a naught then the time it   takes for me to go to half of a naught is t half
one which is the first half life why is first half   because a naught is the initial concentration
i am starting with now when i go from half a   naught to half of that
 so if now half a naught
is my initial concentration right and then i   am going to half of that which is one fourth a
naught then the time taken for that is t half two
 so it is my second half life then again
half of one fourth a naught which is one eight   a naught the time taken to go from one fourth
a naught to half of one fourth a naught which   is one eight a naught is my third half life
t of three ok
 so as you can see from this   kinetic profile you will be able to figure out
based on the manner in which the concentration   of the reactant is decreasing where the first
second and third half lives would be generally   when we say half life you always be in the first
half life that's what talking about unless and   until it is specifically mentioned to you you know
go for the subsequency the second half life or the   third half life and
 so on the first half life
is the one we generally consider and thats what   we will mostly focus on and when i say half life
thats typically what i mean the first half life   right
 so yes from this you know kinetic
profile what we now know to do is   given the starting reactant concentration given
the manner in which it decreases the concentration   reaction decreases as a function of time we will
be able to figure out from this experimental curve   what my half life would be now what is the
significance of this you know why why we   consider this to be a preliminary check
it would not be clear right now to you ah   it will only become ah more clear or clearer
if i ah start discussing about the integrated   rate expressions or the integer rate laws and
then bring this consider half life ah in and   make the connection but at least let me tell you
this if you consider you know this kinetic scheme   though it is not drawn to scale but what you
would realize qualitatively that this t half   one is equal to t half two is equal to t of three
which means that no matter no matter at what point   of this reaction you are the half life is always
the same that means the half life is independent   of the concentration of your reactant right
so let me you know write this again what i am   saying out here is remember we said that the

half life can be a preliminary check what did   i mean by that what sort of insights can i get
by looking at the way the half life is changing   as a function of the progress of the reaction
right
 so what i mean is what i mean is this   that if it has to be a primary check i need to get
something out of it if you look at this the t half   one is equal to t half two is equal to t half three right if this happens that
means the half lines are all equal   if that is the case then what
we say is this is a unique signature of a first order reaction ok its a unique signature of first order reaction so   that means if the half lives are independent of
the reactant concentration it remains the same   throughout right does not matter at what point
of the reaction we are in hence if we can figure   this out we can immediately say without doing
anything else that this is a first order reaction   ok with respect to the reactant hopefully i have
realized that this half life can be very important   as we said that the successive half lives right so
these are your you know you can say these are your successive half-lifes which are equal to each other   being the signature of the first order
equation and as i said it is independent of   the concentration of the reactant
 so when
we go and discuss about the integrated rate   equation for the first order ah reaction we
should be able to see this again right ok now lets move on to the thing we started with the
integrate rate expression
 so lets start with   one of the simpler ones which
is a zero order reaction ok let us start with this now this obviously very simple
 so what we say is that as per definition   of the zero order reaction the rate the rate of
the reaction is equal to k if a is the reactant   k times consideration of the reactant raised
to the bus zero a being the reactant ok
 so this   anything raises one zero is equal to one therefore
rate is equal to k let this be equation one um   ok now also also from the definition of a
rate it is very important to understand that the way the rate is defined is minus d a over
d of t ok this is my definition of the rate   what i am saying i am considering a reaction where a is going to be   ok now this minus d over d of t then
is equal to k let this v 2 right now   what we will do is we will say that ok then i can
write this again as d of a is equal to minus k d t
 so i have two sides two variables one
is depend upon the consideration of a   the other one is depend upon the variable t which is time okay
 so what we will now do is we will integrate both
sides we will integrate both sides
 so which means d of a is equal to minus k d of t and what do

we integrate in between we indicate between t   is equal to zero t is equal to zero that means
the initial time reaction is not yet started   or just about to start with t is equal to t so
this is my interval
so for the time my initial   time point is zero and the final time point is any arbitrary time point t ok then what about the   limits of the integration for a there is a
constant of the reactant
so time zero i say   the concentration of my reactant which is my initial concentration is given as a naught not   corresponding to t is equal to zero then as i go
at time t i can say that my concentration of a   can be represented as t
so if that
is the case then i go ahead and do   the integration keeping in mind that k is a constant let this be equation four   k is a constant and can be kept outside the integral right and can be kept outside the integral if that is
so then
immediately this what this becomes is see i integrate this the first one
on the left hand side it would be a t   minus a at time is equal to zero is equal to
minus k then it would be t minus zero right ok   or i can write it again as a t minus a naught
my initial reactant is equal to minus k of t or a t is equal to a naught
minus k t let this be five ok
so what does this tell me this tells me that
once i have integrated once i have indicated   my what did i start from my zero order reaction
with a going to be once i have integrated that   and i have set up my equations like this then
i did the integration within the defined limits   right a definite integral within the defined time
limits for t is equal to zero my concentration is   a naught the initial concentration for t is
equal to t my concentration is consideration of a   at time t as defined by this integral right
and hence when i go ahead and do the integral   i end up with an equation like this the
moment you end up with an equation like this   you still realize oh this is a straight
line equation right doesn't it look like y is equal to m x plus c right where
y is a t c intercept is a naught   x obviously is t and m is equal to minus k so
y is t c is a naught x is t and m actually is   minus k right
so this is the equation of
straight line if i want to plot a graph   how would the plot look like
so the plot
would look as you have rightly guessed if this is a this is time ok here consideration of a at time t is
equal to consider a naught minus k t
so this would be a straight line straight line with the significance that this is my intercept which is my
initial consideration a naught   because this one corresponds to
time t zero and then the slope the slope is equal to minus k

based on based on the equation a t is equal to a naught minus k t
so this
is the equation i have plotted out here right the equation of a straight line with a
negative slope because the slope is negative the because the slope is negative the negative
slope is equal to minus k and from there i get k
so i get the rate constant ok and
one more important thing is that if for a reaction if for a reaction this
profile is maintained that means if plot of the constitution of a versus time t
is a straight line straight line as we see with the negative slope then then
this is the signature then this is the signature of a zero order
reaction ok
so then this is the signature of a zero order reaction now this is
extremely important to keep in mind ok so you might be you might not be given anything you
just might be given a graph plotted like this and you might be asked what type of a reaction does it
signify and that is what you have to say or that is what you have to keep in mind while you give
the answer
so which means again that if it is zero order kinetics or the reaction you are studying
follows zero order kinetics then the plot of a versus t there is a consideration of a at time t
versus the time t should be linear like this and as i said again the slope being negative by itself
this is equal to minus k right and hence you get k which is a positive value the rate constant
right and that is why this graph is giving you ok
so that was about you know the indicated rate
expression and the plot plots are very useful for chemical kinetics because as i was saying
even for a half life plot even in a half life from a kinetic reaction profile or the plot
from a zero order reaction you would be able to figure out what type of reaction you are talking
about ok now lets consider the half life right
so lets consider the half life for a zero order reaction let us consider the half life now
so we discussed half life before ok let me see what ah my initial the ending equation was ok
so the ending equation was five
so the next equation number would
be six i often you know ah miss or lose track of my equation numbers but anyway let
us consider the definition of half-life now right
so the definition was like this if my
initial concentration is a naught then the half-life which is my first half-life and i said
the half life we are going to refer to is always the first half life is the time it takes to go to
half of a naught right that was the interpretation or that was the definition of half-life

so let us
go back to this equation five where we had a of t   is equal to a naught minus k t
so this was
equation five form right
so now what happens at t   half what happens at t out that means if this t is now t half because i am trying to figure out the   expression for half life from this rate equation
right if i trying to do that what i say is that ok   at t is equal to t half at t is equal to
t half
so this remains the same a naught   is always my initial concentration at
t is equal to t half
so my half life   what changes is in this equation is one is t
is replaced by t half and the other thing is a   gets replaced by half that is a t gets replaced
by half a naught because thats what the definition   of t of s
so tf is what tf is the time it
takes for the consideration of the reactant   to go to or to fall to half of its initial value
or half of its starting value
so you keep this as   six you know once we have this we can
easily rearrange and write that k t half   is equal to a naught minus half of a naught right and
so based on this i can go forward and write
that t half or k t half is equal to half a naught right
so a naught minus half
a naught is half a naught and hence   t half is equal to a naught by two k
so this is a very important relation for the half life
of a zero order reaction speed seven what does this tell you what it tells
you is the half life is directly dependent upon   the concentration of the reactant
so greater the
consideration of the reactant greater than of life   now why do i say it is only depend on the
concentration react well it does depend   upon k but do realize that for a given
reaction k at a certain temperature is   constant and two is obviously a constant right so
essentially what i am going to say is essentially   it is depending upon the concentration
of a naught
so this is what we can write the half life the half life for a zero
order reaction is proportional to the concentration of the reactant right is proportional to the concentration of the reactant so
that means higher the concentration higher   the half life lesser the concentration lesser the
half life right that means again based on this higher concentration means higher half life ok in other
words as a reaction proceeds and if that reaction is of zero order
here we are talking about zero order   reaction right now because everything is under the that description of a zero order   reaction
so as a reaction proceeds and
if it is following zero order then the half life also decreases then the half

life also decreases
right which makes sense again because what happens is the reaction proceeds
what happens is
the reaction proceeds is that my concentration of the reactant is decreasing
right now you can take
a naught you know you can take this a naught like a naught going to half a
naught right and half
a naught what has happened is it is already less than a naught right now if
you go from half
a naught to one fourth a naught see what is happening is you are decreasing it
even more half
a naught is less than a naught one fourth a naught is even lesser than half of
a naught right
so what
it means is if you are going to calculate t half right then t half the first
half life would be
having the maximum value when you go to t half two which is the second half
life which is the
time it takes for you to go from one half or half of a naught to one fourth a
naught because
the concentration has decreased from a naught to half of a naught the half
life will also decrease
ok and
so on and hence as the reaction proceeds the concentration the reaction
decreases
and
so does the half life this is very characteristic feature of a zero
order reaction now recall our concept of recall or concept of half life being
used as a preliminary preliminary check ok and this is what was meant
so what was
meant was that for the zero order reaction for the zero order reaction if it is
zero order reaction if it is zero order
reaction then as the reaction proceeds the half life decreases if you have
so now conversely
if you are given a reaction profile right if you are given a kinetic profile
and from there
you are seeing that the half life is decreasing as a function of time that
means
as the reaction is progressing then you immediately say that as a preliminary
check because the half life is decreasing as the reaction is proceeding it
means that it
should correspond to a zero order reaction or that the reaction i am looking
at follows
zero order kinetics right hopefully now you know having discussed half like
before we
started this integrated rate laws or integrate equations that i was telling
that half life can
be used as a preliminary check then we moved on to the zero order integrated
out got this
linear dependence of the concentration on time negative slope from the slope
is this you get
minus k and hence you get k being a positive quantity but then you see half
life it decreases
as a reaction is progressing and then it tells you as again a preliminary

check i am using this word
each and every time having not done anything else just using the half life you are able to take
tell that this reaction must follow zero order kinetics ok
so you can see that ah you know today
in this class we have entered this ah realm of integrated rate laws or indicate rate equations
we are done with the zero order rate equation so what we will do is in the next class we will focus
on the first order and second order rate equations and then again move on from there and discuss the
other aspects of chemical kinetics ok thank you you