welcome to this lecture this
would be a lecture number eight   on chemical kinetics and again as we do every time
quick recap of what we covered in lecture seven   ah
 so you know we had started looking at
these integrated rate equations and before   looking at an example of the same we had
introduced the concept of half life and we had   even said that this half life can be treated as a
preliminary check of the type of reaction you have at hands or the type of reaction you are studying
right and then we moved on ah to the first   example of our rate of an integrated rate
equation which was that for a zero order   reaction
 so remember when what we did
was you know for the zero order reaction   we took an equation like this right and in this
equation what we did was we had this a going to   p right and then we set up the rate equation as is
seen here
 so the most important one being minus d   of a over d of t is equal to k then we went ahead
and ah integrated we ended up with something like   this ok we ended up with something like this
where when we are integrating between limits   t is equal to zero we have ah concentration of
a the reactant to be its initial concentration   a naught and then at t is equal to certain time
t the concentration of a would be consideration   a at time t
 so we go ahead do the same and
what we end up with is this characteristic   rate equation for a zero order reaction
 so this
is again the signature of zero order reaction   what does this mean what it means is that if you
would plot the concentration of a at a given time   right against time or versus time you will
be getting a straight line because this is an   equation of the type y is equal to m x plus c and
this equation ah our the plot would be having a   negative slope because your slope in this case
is minus k
 so this is what we plotted last time   as you can see the intercept would be a naught
and the slope is minus k right again if you would   read what is written out here only if the
plot of concentration of a as a function   of time is a straight line then this
is definitely a zero order reaction   from the plot what can you do or what can you get
you can get the intercept which would give you   the initial concentration a naught
and you can also get the slope that   means from the slope you will get the rate
constant because slope is equal to minus k   and hence it will give you a

positive value of the
rate constant again we ended the class with this expression for the half life of our zero order
reaction
so what we did was as the half life was defined t of half is that time at which the
concentration the initial concentration falls to half of its value
so the initial concentration is
a naught the half of it would be half of a naught right we put it back in the equation the rate
equation for the zero order ah reaction and this is what we ended up with and the final expression
for the half life was this where t of f is equal to concentration of a naught over two k
so what
it means is the half life is proportional to the concentration of the reaction or the initial
concentration of the reactant in other words in other words what it means is what it means is that
higher the concentration higher is the half life as a reaction proceeds your concentration
is decreasing your half life is also decreasing and this would be another
signature of a zero order reaction which then brings us to this feature of a half life
where we had said that the half life indeed can be used as a preliminary check of the type of
reaction you have at hands ok
so we stop there and what today we will do is we will
you know we will start with what we commonly refer to as the first order reaction right
so in the first order
reaction we would again take this reaction a going to p okay i will just check the
number of the last equation i had used
so that i can start from there okay the last equation number
was 7
so i will start from there now for this as its being defined the first order
reaction then i can write the rate is equal to k the rate constant times the
concentration of a ok
so let this be eight
so in continuation from the zero order reaction example
so if this it what it is then from the equation or the reaction out here what we can write is
that minus d of a over d of t is equal to k times the concentration of a right
so once you have set this up then it is very
straight forward the key point is to set this expression or this equation up ok once you
have this then we go ahead and we write that minus d of a
so this is what we had i am writing
it again is equal to k times concentration of a
so this was equation nine
so if you are having
that what will now do is will bring a on one side and take d t on the other side

so that is
we are going to have a over a is equal to k d t right and then we move forward and we integrate so
what we will do is we will integrate again between some well defined limits will take
the negative sign on the other side is k we can integrate it like
this again at t is equal to zero again a t is equal to zero the concentration out for a would be a naught at t is equal to the t the concentration of this would be t ok remember
this k is a constant
so it can be taken out of the integration and hence we have this so
now we go ahead and integrate
so on the left hand side you realize that this is your
standard integral involving your natural log
so then what you get from here is
so what you get
from here is based on this i write natural log a t the natural log is log base e minus natural log a naught is equal to minus k t right so
this can be again written as natural log of a t
so let this be ten is equal to
natural log of a naught minus k t eleven right
so the other way
of writing this equation is that again if i you know if i write it from here if i write from here i can write it as natural log a t over a naught is equal to minus
k t right
so there is this be twelve ok and then what i can do is i can go ahead and write like this a t over a naught is equal to e to the power minus k t okay let this be 13
and finally what i can write is
so this e being meaning exponential minus k t that is the order of the exponent out here and then i can write a t is equal to a naught e to the power minus k t or some other way of
writing is a of t is equal to a naught exponential minus k t ok
so let this be 14
so this is your rate equation for
a first order reaction
so please again let us go back and take a look at these
so we
started with this we started with this where minus d of a over d of t is equal to k times a k
being the rate constant then we rearranged
so that a came to one side the t went to the other side
we integrated between the limits what were the limits at t is equal to zero i would be having the
concentration of a as concentration of a naught at t is equal to t the concentration of a is given
as concentration of a t outside the large brackets we integrate it within these limits right the one
on the left hand side is a logarithmic integral at standard integral the other on the right hand side
is just k times t okay and hence what we get is an expression like this right
so natural log of
a t minus natural log of a naught is equal to minus k t if you rearrange this

chemical
in this form then from ten i get eleven right the other way of doing it is instead of
keeping it in the form of eleven i go ahead and express it in this form where natural log a
of t over a naught is equal to minus k t what this tells us is that the expression can now
be rewritten as concentration of a of t over constant a naught is equal to e
to the power minus k t from where i get this expression where a of t is equal
to a naught e to the power minus k t or a of t is equal to cos a naught exponential
minus k t what does this mean what it means is if you you know focus on this equation what it
means is that you know equation 14 it says that concentration of a naught is what consideration
of a naught is the initial concentration t is the time that has elapsed since my reaction
has started what is k k is the rate constant ok and you immediately realize that what
the equation is trying to tell you is that the concentration of a at time t is what is
essentially an exponentially decaying function that means the concentration of a naught
what would happen the concentrator a naught or the concentration of a from a naught would
decay exponentially as a function of time right and what is the nature it is always exponential
but what is the rate
so rate is given by the rate constant
so k t what it is telling you
is that this exponential function would decay a naught you start from a naught it would
decay like this right exponential and the decay constant the decay constant which will come back to later
so just you know hold on ah to the thoughts
this concept this d k constant is your rate constant which is k right ok now
what can we do with this ah you have seen ah different variations of the same equation let
us take ah you know these variations one by one
so for example let us go back to this
variation which was the one we you know said was equation number eleven
so from equation
number eleven if you write this one down again right
so let us write this one down remember we
are still talking about a first order reaction a naught minus k t
so this was our equation
number eleven
so what this thing is again immediately epstein is that oh this is
the equation of a straight line right
so this equation of straight line which means
if i have a plot like this right if i have the natural log of my concentration out here
if i have the time on this axis the x axis and if i plot it now if i plot it now i will be

getting a plot which will look something like this a straight line right and from the
straight line what are you going to get
so one is i get the intercept what is intercept the intercept is this and from the slope this is equal to minus k right
so the slope
is negative this is equal to minus k and hence from the slope we get the value of the rate
constant which is k
so this is the rate constant how you get the rate constant for a first order reaction if you plot it like this ok
so the other way of saying this is the signature of a first
order reaction is what the signature of first order reaction then you know can be written
like this that if you know i can write this as if the experimental data is the experimental data fit first order kinetics if the experimental data fit
first order kinetics then the plot of in an a t against time will be a line will be a straight line as we saw that is linear with the negative slope obviously and from the slope what you would get is the rate constant slope is equal to minus k again
slope itself being negative the negative signs cancel out and then you get the value of the rate
constant
so please remember that this is important the plot of this quantity
right log base e of a forces time or against time has to be a linear plot with the negative slope for the reactant this was one way of looking at it or at least ah you also understand that if you are encountered with a plot which has
this characteristic then immediately you can pin it down and say that yes this is a reaction
which follows first order kinetics great now let us talk about half life like we
did for the serial order reaction
so you know let us talk about
this
so when you know when we do this half life remember what was half life we said the half life which is denoted by t half is what where the initial concentration a
goes down to half of a naught right
so that means you start with initial concentration
a naught and the time it takes to go down to exact half of the concentration is your t half now
what is the expression for t half right we can you know again get it multiple ways
so suppose i you
know do it from this equation where i knew that natural log a t over a naught is equal to is
equal to minus k t and if you would remember and if you remember this was get written before
equation number twelve
so again i will write this was equation number twelve now suppose
i have t half then when i am saying t half then when i am saying t half then i
can write natural log a this would be sorry let me write again let me write it

again
let me write on the next page
so when i am saying t half remember i am considering half life i am
saying at t half right then this is natural log the concentration of a at what
time
at time t is equal to t half over a naught is equal to minus k t where t is t
half right ok now by definition by definition t
half is what that point or that time where the concentration of a naught has
become half of it or
half a naught
so then i can write natural log half a naught over a naught is equal to minus
k t half
isn't it
so obviously there now then you realize this a naught a naught cancels out if
this a
naught a naught cancels out i will be having half is equal to minus k t half
right
so let me see what was the last equation number
so i can put the equation
number n that was twelve i think it was fourteen
so let this equation number be you
know fifteen
so let this be sixteen ok from here from here what would i get
so what
i get was you know from here what i get is i can immediately write that
hopefully you will realize
from here i can make this transformation to go to t half is equal to what i am
sure realize is
two over k right and this can also be written as what t half is equal to zero
point six
nine three over k
so this is seventeen eighteen
so this was the working equation
for calculating t half see even if you forget even if you forget that means
you there is no need
to memorize as long as you understand the steps that have been taken to
calculate t half that is
you know the point i am trying to make out here then once i do this the
natural log
of half is equal to minus k t half right and from here i am sure you will
realize
that what i get is the t of f is equal to log base e two over k or t of of is
equal to zero point six nine three by k
so now what you have done is you have got an
expression for t half for a first order reaction right you have got an
expression for tr
for a first order reaction how is this different from that of a zero order
reaction
you see in this expression for t half there is no concentration term there is
no concentration
term
so this t half is a constant is equal to 0.
693 is a constant over k which is a rate
constant which is constant for a given reaction right

so which means is which means is that we
can write the half life we can write the half life for a first order reaction
the half life for a
first order reaction is independent of the concentration of the reactant ok
so again the half life for a first order
reaction is independent this is the keyword the half life for a first order
reaction
is independent of the concentration of the reactant that is it takes the same
value
this t half takes the same value no matter what the extent of reaction
is
so again i write that means t half takes the same value no matter what the
extent of reaction is right
so t half takes the same value the same value no matter what the extent of the
reaction is
so it is immaterial at what point of the reaction you are you try to get t
half say
from initial to half of it or from t half to half of that which is t one
fourth like you were
doing t of one t of two t of three or to go to one eight of a naught right
which is third t half half
life all of these t halves all of these t halves have exactly the same value
why because based
on what you have derived it has no dependence on the concentration that is it
does not show any
dependence on the concentration of the reactant rather it is a constant which
is given
by 0.
693 by k again 0.
693 is a constant k being of that reaction is always a constant
so t f is a constant
so again if you would remember that when we were discussing t half even
before we had started with the zero order reaction i had shown you a plot i
will show the plot
to you again where i i told you that the fact that these t halves are equal
might be a signature
or is a signature of a first order reaction and that is what you have shown
right now by doing
a quick derivation starting from your integrated rate equation okay
so this is the power of t half
right again its a preliminary check
so if your t of is constant throat it tells you that it is
a reaction following first order kinetics great now lets look at something a
little bit different
or you know before before that lets ah take a small example now when i take
this example just
be careful of what we are discussing right now because it is a first order
reaction but with
a slight difference
so what i mean is you know for example take this following
decomposition reaction
so two n two o five going to four n o two gas plus o two gas ok
so this is the reaction i am following
so when i am following this reaction i am told that this reaction also follows

first order
kinetics that means rate is equal to k times   into five
 so the decomposition of n two o five
is following a first order kinetics right now   think about the derivation of the rate equation
the integrated weight equation based on this   now when i write
 so you do exactly the same thing
you know that rate is equal to k times n2o5 now   also the rate of the reaction the rate of the
reaction from the stoichiometry is given as   minus one by two that nu of the reactant nu
being the strike of a stoichiometric coefficient times d of o five over d of t let me write again
is equal to minus half right d n two o five over d of t ok
 so this is my expression for the rate ok
in terms of the disappearance of n two o five now   if i try to derive that means if i try to get the
integrated red equation for this this is what i   will do right what i will do is i will equate this
one and this one right i'll equate this one and i   liquid this one as we did before
 so when i do that
see there is a difference coming in the difference   is like this i write now minus half d of n two o
five over d of t is equal to is equal to what k   into o5
 so this is my equation right now let
this be equation number nineteen now again i go   and do exactly the same thing but then a small
difference creeps in if you would keep track   of what i am doing
 so what i do now is i say
that ok this is d n two o five over two o five but i have a two out here isn't it
 so i will
write it as minus two k d of t once i write   it as minus two k d of t then what i do is i
integrate what do i integrate i integrate again   between the limits what are the limits
 so the limits are   n two o five the initial concentration at t
is equal to zero then this is n two o five   at time t this is at time t ok again
exactly the same thing as we did   last time just keep track of this fact that here k is a constant
 so is two
 so it's true
 so this two k can be taken out of the integral
sign and then what we go ahead and write is that ok
 so i will write straight away natural log n two o five t minus natural log n
two o five zero is equal to minus two k t or or   ln n 2 o 5 t is equal to ln n 2 o
5 0 minus 2 k t right now what is the thing that i am i am trying to drive at so
let this be equation 20.
 compare this equation   compare this equation with the equation we had
derived before which was equation number eleven

so this is equation number
eleven that i had before   where see if i move it here this is the question number four if you read at the bottom of the   slide
so ln a t is equal to ln a naught minus
k t now this reactant has become n two o five   right at time t is equal to ln n two o five naught
initial concentration minus two k t the difference   you see out here is that here i have a two k a i
have a k right as such everything remains the same   the only problem being here i had that
stoichiometry out here for n two o five   when i derived it i said a going to p here
i am saying its two a go into your products   right
so hence that stoichiometry has to be taken
into consideration and how do i take that into   consideration is well first of all i had done this
derivation i know that this two is coming in to   the picture
so now what i will do is only i keep
track of this and then if i would be having a plot time and this is n two o five if i would be having
a plot of this right when i plot this you see   what i will get is something like this again a
straight line right sorry this is straight line
so what would my intercept be my intercept again would be natural log n two o five the initial
concentration but look at the slope look at   the slope now the slope is equal to minus
two k the slope is equal to minus two k   this is what is important
so that
stoichiometry which appeared in that equation   right the stoichiometry which appeared in that equation here where two n two o five goes to four n o
two plus o two this stoichiometry it has to   appear right it has to appear stoichiometry is
important
so where did it appear
so it appeared when you were trying to calculate the slope   then if slope is equal to minus two k then
you write then k is equal to slope over minus two right
so this is how the reaction
stoichiometry is taken care of right i hope i   have been able to put this point across that when
you have the stoichiometry coefficient you say nu   j or whatever is equal to one it does not matter
right because it the slope is equal to k but the   moment it is different from that the moment it is
different from that this is what comes in thus i   can you know i can generalize it right
so that
ah it is easy for you to remember easy for you   to apply
so to generalize what i can write is
if for any reaction i have
so to to generalize to generalize if for any reaction right
i have say two a go into products or   this was for n two of five i can say a a go into

products where a is the stoichiometric coefficient right
so the moment i have that then i write that
the rate is equal to minus one by a d of a over d of t right this is equal to k
times concentration of a being a first order reaction and when i go ahead and do the integration what i end up with is that natural log of a right t is equal to natural log a naught minus minus a k t this is extremely important and i would give this this twenty one
so here is an extremely general form of your
integrated rate equation in the linear form for a reaction following first order kinetics where a is the stoichiometric coefficient in
front of the reactant if a is equal to one it falls back to equation eleven if a is
not equal to one then just use this great yeah as i was telling you there is uh you know
one more important thing that we talk about ah often when we consider first order reaction
that important thing though is it is a little bit beyond ah your you know your syllabus
right now but i think because we are talking about first order kinetics its highly important
that you keep this in mind right what we say is something referred to as a relaxation time ok now do not worry about it its actually
very simple the relaxation time is given this symbol tau
right
so this symbol is tau ok now what do i mean by the relaxation time so
suppose i have an initial concentration for a first order reaction the initial concentration
a naught right i am still you know sticking to the reaction a going to p right
so a naught then
a naught at a certain point of time the a naught concentration is decreasing from a naught and
i get a value of a naught which is like this what is it
so at a certain
time at a certain time t at a certain time t this a
naught is equal to 1 by e times concentration of a naught ok now this
one by e concentration of a naught is ah important y
so one by essentially
is the inverse of your e right but what it tells you is that the time it takes the time it takes for a naught to go there to one by e of its original value is referred to as the relaxation time right which can be symbolizes stop
so again
what is the relaxation time
so the relaxation time is nothing but for a naught to decrease
to that concentration which is one by e of its original value
so what was t half t offers that
concentration or that time it takes to decrease to half of its original level that is half a naught
so relaxation time is that time it takes to reach a concentration which
is one by e of its original value and if you remember what the value of e is
then one by e is nothing but can be written as a naught is equal to this one by e
right when we say a naught is equal to zero point three six eight a naught ok

i
would say this is at time t is equal to top
so when a is at a at time t is equal
to two is equal to zero point three six eight a naught ok
so what has happened what has
happened is that at time t is equal to tau so let me write again at time t is
equal to tau the concentration of a is 0.
368 a naught ok
so what it means is that after this time tau
has elapsed after this time tau has elapsed it has decreased to 0.
368 a naught
that means what i can write is not just follow this what i am writing
is that at t is equal to tau which is the relaxation time at t is equal to tau
which is the relaxation time the reaction has gone to the reaction has gone to
sixty
three point two percent completion sixty three point two percent completion
until and still has how much to go 36.
8 percent to go right
so again what is this relaxation time
this relaxation time is that time where the concentration of a at t is equal
to tau has
decreased to point three six eight of a naught and in words it means that the
reaction has gone
to sixty three point two percent completion and still has and still has thirty
six point
eight percent to go
so that is the definition of a relaxation time ok like we found an
expression
for t half we can also find an expression for this relaxation time it is very
easy what we do is
we we recall this equation where you know we had consideration of a at time t is
equal to
consideration of a naught e to the power minus k t right this was equation
number
fourteen for us if i remember correctly now what we are saying is at t is
equal
to tau right the relaxation time this a of t is what
so at t is equal to tau this one is
one by e a naught
so one by e a naught is equal to a naught e to the power minus k t right or i
can
write one by e is equal to e to the power minus k t by canceling a naught from
both sides or i
can write e to the power minus one is equal to e to the power minus k t
so this is remember
this is t is equal to tau
so now i can write e to the power minus one is equal to e to the
power minus k times tau where i have replaced t by tau because tau is the
relaxation time
now then once i have this
so if this is say fifteen for me then i can easily write this one
as e to the power one is equal to e to the power k tau right or i take natural
log on both
sides or i can write straight from there it does not matter this is equal to k

tau right hence this is one on this
side
so i can write k tau is equal to one or what is tau tau is equal to one by
k right or tau is equal to one by k so this is an expression for the
relaxation
time and let this be i forget oh sorry so i missed out the equation number
just hold on let
me see what the equation number this one would be ok
so i guess this one would be having you should
just let me check one thing
so i have generalized ok
so this one would be having equation
number of 22.

so please change this this one will be equation number
22 and i can say this one is twenty three
so the way the relaxation time was defined
it was defined that it comes down to one by e of its value right
so one by e of a naught
so once
i know that this relaxation time corresponds to that concentration which is
one by e a naught i
put it back in my integrated equation trying to find an expression for tau
which is relaxation
time i go ahead do it and then i end up with a very simple expression for tau
which is equal
to one by k that means what is tau c tau is units of time whether its minutes
seconds hours
and
so on remember k what is k for a first order reaction k has the units of
inverse of time and
it makes sense that tau is equal to one by k even in terms of units right
so the inverse of k would
be your units of time the only thing you have to keep in mind the only thing
you have to keep in
mind when you are talking about relaxation time ah this is the only thing you
need to know
relaxation time it becomes ah handy in many cases well as i was telling you
the only
important point is that this relaxation time is only applicable
so tau or relaxation times are only applicable for first order or pseudo first
order reactions ok
so sorry its relaxation
so reaction times
are only applicable for first order or pseudo first order reactions this is
something you would like to keep in mind i
will end this section on ah first order reactions by this plot
so that you can have a better
feeling of what we have discussed up till now
so the plot you know goes like this
lets see whether i can draw it properly ok
so here what i am having is i am having well
lets say this i mentioned this is my time ok this my time this is my
concentration reaction

on y axis what i say is this is my 100 percent okay hundred percent hundred percent means i have
so this is zero time
so i have hundred percent of the reactant no product there is my initial value a naught
so which i say is hundred percent right now if you remember that one of the expressions ok
so one of the expressions for let me bring this one back yeah one of the expressions for a first order reaction was this that the concentration of a how does it change as
a function of time it changes as e to the minus k t and when t is equal to zero the concentration
is a naught right
so that is what we are doing here
so at t is equal to zero the
concentration is a naught which is hundred percent
so i am saying that that is normal is 200 percent
because that is the maximum i can have
so that is hundred percent right now it is going to
decay exponentially
so let me try to draw exponential decaying function now let us
see can we do something else with the graph based on the discussions we have had until now
so what is t half t f is that part where this one would decrease to
say fifty percent
so this is fifty percent
so this is i i say this is percent right
so that is ok
so sorry this is ah yeah this is percent right so percent of ah you know reactant remaining
so when
i say fifty percent its not exactly drawn to scale then what is this
so this is my t half this is my t half right now remember the
relaxation time what is the relaxation time to say the relaxation time said that i would
decrease here i would decrease to what value i would decrease to about sixty three percent of
my initial level that means the reaction is gone to the extent of sixty three point two percent so
if i do that if you know i say that this is about that you know sixty three percent
right then i can say that from here if this is say 63.
2 percent two roughly ok then this tau or this t
on this axis would be referred to as what would be referred to as tau
so if i go from
well i let me do it here it is easy for me from here to here this would be tau ok
so this
would be tau
so this is my relaxation time
so you realize that even after this time is
uh significant now there is you know ah about the rest of the reaction ah 36.
8 percent of the
reaction has to go on okay it is not exactly down to scale but hopefully you

understand the point i
am trying to make is that from this graph we can figure out what the
relaxation time would be if i
am given a plot like this right now what about the other t halves
so see
so from fifty percent zero
i come down to say another half somewhere here right
so that would be twenty five for
me
so if i do 25 and again if i try to make some sense
so this would be the other t half
for me
so from here to here
so if that is you know t of one
so this would be another t half
so this is another t half from here to here t half is another t of the next t
half t this t half
and the first t half which was from here to here aren't they the same though
it is not
drawn to scale but aren't they the same again if you go for the next
so this is ah
if i say this is t half one this is t half two essentially ok this t of two
from
here to here then if i go to t of three again that stretch it would be
equidistant
that means they would exactly be the same
so what this plot is telling
you its telling a lot of things first if i am going to plot the concentration of
a as a function of time
this is what i am getting right a zero is hundred percent starting from at
time t is equal
to zero is a naught which is hundred percent right as time goes on how does
the concentration of a decrease it decrease exponentially as a
function of time is exponential factor right now when it comes to 50 percent
it would
be t half
so if it is fifty percent is t half then i can say that this fifty percent
should
corresponding to my first t half which is half of a naught right now from
fifty percent if i take
another t half i should go to twenty five percent which is here which is
essentially one fourth
of a naught
so this twenty five percent
so from fifty percent twenty five percent is my
second t half and you can say this t half and this t half they are exactly the
same why
because t half for a first order reaction is a constant right now look at the
relaxation time which is given by this
so what does it mean it means that the time it
takes for it to decay to about 63 percent of its initial value that is my
relaxation time
so this
is where sixty three point two percent is and if i read of the corresponding

time from the time
axis that would be my tau which is my relaxation time right hence from this first order plot
you can actually or this ah exponentially decaying plot you can read of a lot of things
so this was the end with ah you know the first row kinetics and next class what we will do is
we will start with second order okay thank you you