so welcome to today's lecture
 so as you can
see this is a lecture number nine on the   topic of chemical kinetics today what we will
do is remember yesterday we were dealing with   first order rate equations and you know the
derivation of the indegree law of the same   and some characteristic features of ah first
order rate equation what we also introduced was   along with ah you know all the general things
was the concept of relaxation time and how the   relaxation time can ah you know the expression
of the same can be obtained from the integrated   rate equation
 so today we will move one step ah
further what we will do is we will have a quick   look at ah second order equations
 so for second
order equations you know everything remains the   same only that it becomes ah second order okay
so lets you know talk about then second order reactions that is reactions that follow second order
kinetics
 so we will go back to a general   reaction is always like this a going to p right
and here we say that the rate r is equal to k a square
 so once you know we have this then
what we do is we go ahead and try to derive or   derive the rate equation
 so again
rate you know is expressed as minus   d of a over d of t
 so we have two sides of the
equation
 so one side is this the expression of   rate in terms of the change in concentration and
the other side is this as the rate expression   would give in terms of the concentration
of a raise to the power two this being a   second order rate equation ok
 so you know in
this case what ah i will do is i will ah just   go ahead and start with this say this is one and
this is two ok for this second order reaction
 so now what we do is we equate both sides so
what we do is we say that ok now we have this two   different expressions for rate and we say that ok
minus d over d of t is equal to k times a squared   right
 so let this be three again as usual as
we have done before we bring a on this side ok we take d t to the other side now we
integrate
 so within the limits t of a over a squared is equal to minus k d t so
what are the limits again remember t   is equal to zero then this would be a
0 when t is equal to t this would be   a t okay
 so this a t remember as we have been
using this term before having set this up   you are almost there
 so you just integrate these

are standard integrals remember again on the right hand side you have k which is a constant the rate constant it can be taken out of the integral right so what you are left with is based on this what you left with is then i have 1 by a t minus 1 by a naught with a negative sign is equal to minus k t ok because thats what you are doing you are doing a standard integral remember so there would be negative sign so this two so n is equal to minus two minus two plus one and the negative sign out up front and then you have the negative sign out here right and then this is coming from the integral one over consideration of a at time t minus one over concentration of a at time zero or this is the initial concentration this is equal to minus kt so i can cancel the negative signs from both sides and then i can rewrite this as one by a t minus one by a naught is equal to k t or this is the final form one by a t is equal to one by a naught plus k t and let this be number four so this is the final form of the rate equation for our reaction following second order kinetics second order kinetics based based on the fact that you are talking about a single reactant a single direction means like this where a is going to p a this is a single reaction there is no other reactant in place right it is not like a plus b it is only a going to p and then the rate is given as k times a squared signifying that it is a second order reaction its only under those conditions is this equation value now lets try to look at the characteristics of this equation as you can again realize see we mostly try to deal with ah linear equations right so this is also linear equations we have done it for the zero order reaction we have done it for the first order ah reaction we are trying to do again the same thing for the second order reaction so what we see again is a linear equation there is a linear dependence so so what is the linear dependence of so you can see if i go by this equation 4 right and i say i plot reciprocal of a t that is one by a t against time i should be getting a straight line with a positive slope so which means which means if i have a plot like this with time on the x axis as usual and the reciprocal of the concentration on the y axis then my plot would go something like this ok for a second order equation and this intercept is what it is 1 by a naught and slope

is equal to k right this is a
positive slope anyway you directly get k from here ok
so in other words what we can say is that the
signature of a second order reaction is like this that the plot the plot of one by a t the subscript
that is concentration at different times against time is linear is linear right
so the plot of the reciprocal of the
concentration versus the time no matter what the unit is has to be linear only if
it is linear only and only if it is linear we say that this reaction follows second
order kinetics ok good
so what have we done we started from when we start from the integrated
rate equations we first need to use half life right we will do that the same thing out here for
a second order ah reaction or equation then ah we introduce the zero order kinetics
we went for the first order kinetics and we are doing the second order kinetics
right
so lets talk about the half life now
so the half life for ah second order reaction
so we are talking
about the half life out here we know now what the half life means again
so t half is what it is that time at which the initial concentration a naught goes
to half of a naught ok
so that is what t of s
so that is the time taken is the
time taken for the concentration to fall to half of its original value right
so if its
original value of initial value is a naught then the time it takes to fall to half of a naught
is again t half as we always keep on saying so what we will do is to derive the expression for
t naught we will go back to the expression we had from before k t
so this was our equation
four
so what are you going to do here because it is t half because it
is t half then what we will do is this t becomes t half we replace it by t half
right and this a t at t of what happens is this is half of a naught
so these are the only
two changes we make in the equation everything assumes the same you know that is
why or this is the utility of a red equation that you want something you get it from the right
equation because you have you have an equation which reflects the dependence of the variation
of the concentration on time right ok
so we will insert these things in equation number
four to get the expression for t half right
so let it let me write now again so
then what i said was this is one by half a naught minus one by a naught

so i have taken a
naught to the other side is equal to k t half   or i can write k t half is equal
to two over a naught minus one over a naught right or t half can written as one by k a naught
so this
is expression for the half life for a second order reaction what does this you know t half tell
you then
so this t half is telling you its the   time taken to go down to half of its original
value and the expression for t half is given   like this it is equal to one by k k is the
rate constant is a constant but it is also   depend upon the concentration right that means
t half is inversely proportional is inversely   proportional to the initial consideration of
the concentration of the reactant you have   in question
so what does this mean
what it means is we say that the based on t half is equal to one by k a naught
so expression we just
derived we say that half life half life is proportional is proportional to the reciprocal that means one by inverse is
proportional to the reciprocal of concentration what does this mean what it means is larger
the concentration lesser is a half life larger the concentration lesser is the half life
so larger
the concentration lesser is the half life again   this tells you that this is a feature or a
characteristic feature of a reaction following   second order kinetics in other words the final
statement we make about this half life is this
so you can realize that as my concentration
decreases right that means as my concentra as   my reaction is proceeding the concentration of
a is decreasing right and remember we can have   half lives at different times t half t one four
and and
so on and because this concentration is   decreasing what is going to happen and it
is inversely proportional
so your half life   is going to increase right because the inverse reproportion
so what we can say now then is that half life increases as the reaction
proceeds reaction proceeds and this is for a second order reaction in other words for
the second order reaction as the reaction would proceed the concentration
of the reactant would decrease and because this   half life shows an inverse dependence that means
proportional to the reciprocal of concentration   hence the half life should increase so
this again reminds you of this fact that t half being a preliminary check of the type of reaction we have at hands so

lets pause for a moment and think about this t half characteristics remember when we talked
about t half and this was even before we started with the rate equations we said the t half can
give you a guide to what type of reaction you are monitoring or it can be a possible guide and then
we went ahead we started with the zero order what did we see the t half was proportional to the
concentration that means as the concentration would increase
so would t half second we went for
the first order what did we find first order we found the first order the t of is equal to natural
log of 2 over k or 0.
693 over k t half had no dependence on the concentration whatsoever
so no
matter no matter what the concentration is at any point given point of time in the reaction t half
is always the same
so that is the signature of the first order reaction reaction following first hero
kinetics and what we just just derived was for a second order reaction or a reaction following
second order kinetics then t half is inversely proportional to the concentration which means that
as the reaction proceeds as the reaction proceeds the concentration decreases and the half life
increases hopefully now you understand that this t half indeed indeed can be used as a preliminary
check for the type of reaction you are monitoring or the type of reaction you want to study or you
want to investigate right this is the importance of t half or the half life now you realize that
having done these derivations it would be easy for you to ah you know set up rate equations and
derive anything else that you might want to do now if you take a step back and think about what
we have derived right now what we did was this we said that a going to p now remember for
first order kinetics we also did an equi something a general equation where a a is going
to p that means now the rate is equal to minus 1 by a d of a over d of t which is equal to k times
a square isn't it
so what i want you to do is for a reaction like this which follows
second order kinetics right derive the integrated rate law derive the
integrate law and see how it turns out where this a that is the stoichiometric coefficient is
coming in ok now another aspect
so this is one this is one what did we say we said that ok i am
i am still having a single reactant it distinguish still a single reactant case a is going to p that
is what we derived right now now i am saying that ok this a is having a stoichiometric coefficient
a general one you know you know ah general stoichiometric equation which might

be one if it
if a is equal to one then i am coming back to this if a is not equal to one
say if a is equal to two
a visible three whatever then i have this thing that i have to take care of
right and that is
why you derive the rate law now there is another point to this the point is
that yes we have
done the single reactant case a going to b what about having two different
reactants for example having a plus b into b ok what will
happen there now here
so the rate this being a second order
equation the rate would be k times the concentration of a times the constant
of b
so what you told is that you are given a second order equation or
so this equation
follows second order kinetics right it follows this expression rate is equal
to ah k times
concentration of a times concentration of b both being raised to the power one
so one plus
one is equal to two and hence this is a second order equation or reaction
following second
order kinetics good now what happens is if if concentration of a is equal to
consideration
of b right if concentration of a is equal to concentration of b then i
can rewrite r is equal to k a squared
so this is say six is seven now once we have this you realize that
this r is equal to k squared is exactly the same as of having a single
reactant no problem now
this is only applicable or only possible when i say that my concentration of
a is equal to consideration of b however however if concentration of a is not
equal to concentration of b that means if consideration of a is not equal to
concentration
of b then i can no longer write this i can no longer write this
so my r is always equal
to k times a times b
so then my question to you is under these conditions where you
are given that concentration of a is not equal to consideration of b you are
given that the reaction you are following is of the type a plus b going to b
and that it is a second order equation following this rate expression
or rate law derive derive the integrated rate law for a reaction like mentioned
above which means this one where you are given that the
concentration is not equal to concentration of b that a plus b goes to p and
that the reaction is
following second order kinetics where r is equal to k times consideration of a
times consideration
of b
so this is again another problem for you please try it out you will find
interesting as
to what you get ok let us talk about a reaction involving several reactants
like this
so let give
it a separate heading
so this one is a reaction involving several reactants ok several reactants
right

so what we mean
by this is that we have a general form going to p
so let this be say it
so if this is a reaction right where you are
seeing that there is a reactant a there is reactant b right there can be other reactants but
will not make it that complicated what we say that we will just stick to two types of reactants
out here right they having their corresponding stoichiometric coefficients which can be one
or which can be different from one right and we need to establish we need to establish we need to establish whether the rate equation can be written as or is of the form r is equal to k is a reactant ah you know rate constant
a to the power alpha b to the power beta
so this is important first this is a reaction involving several
reactants in this case more than one a and b then a and b they are having their
corresponding stoichiometric coefficient small a small b they are going to
be the products now we are saying that how can we establish or can we establish whether the rate equation is equal to k times concentration of a to the power alpha so
b to the power beta where alpha and beta are the orders with respect to those reactants
so alpha is the order with respect to a beta is the order with respect to b and then
the total order of the reaction would be alpha plus beta right ok now what is the problem the problem is this
so what is the problem the problem
is that the rate the rate of reaction the rate of reaction now depends now depends on the concentration of both the reactions right
so i can not only look at
a i cannot only look at b because the rate is depending upon both right hence if this is a
problem what we face with is that it is difficult it is difficult to separate out the contributions
that means it is difficult to disentangle it is difficult to disentangle that means
is difficult to separate out the effect of one reactant of one reactant from the other again what it means is if
the rate is dependent upon both a and b it is difficult for me to separate out
the individual contributions of these two reactants to the total rate right
so that's why it says it is difficult to disentangle but then you know there are always ways out there always ways to tackle problems like this
so what
we then do is we arrange
so way out what is the way
out
so the way out is we arrange are experimental we arrange our experimental conditions we arrange experimental correlations in such a way we that data analysis will be simplified ok
so what is the way out then the way
out is we devise or design experiment in such a way that we can simplify the

data analysis
right
 so this is the keyword we arrange   or design experiment conditions
in such a way that the   data analysis is not that cumbersome
not that complicated
 so the ways   these you know there are two ways of
doing this
 so the two ways are as follows number one it is referred to as the isolation method and number two
it is referred to as the initial rate method we look at these two ways separately and
then another feature of these rate equations   would come from here ok
 so let us take these
two individually you will soon realize why   ah i am going through this right it gives you a
better feeling of how complicated weight equations   can be addressed or analyzed
so lets talk about this   isolation method to start with right
so let us go back to our initial reaction we are talking about the isolation method remember
the reaction the general form was a plus b   with the corresponding stoichiometric coefficients
going to p let us take this reaction which is c l   o minus aqueous plus p r minus aqueous going
to b r o minus aqueous plus c l minus a cos   right
 so now this is reaction which involves
multiple reactants two reactants c l o minus   b r minus these are the reactants products mean
b r o minus c l minus if you remember i think in   lecture number two or three we had introduced
this ah equation to look at the graphical   representations of equations that means
ah or reactions that means looking at the   kinetic profiles and this reaction was taken
as an example
 so we bring this reaction back   and ah base our forthcoming discussion on this reaction ok
 so now having ah you know   got in this reaction
 so let this reaction well
let us give it a number say nine a plausible   rate equation a plausible rate equation can be
written like this
 so we can say ah plausible rate equation for this one can be written
as r is equal to k c l o minus alpha br minus beta
 so this is a possible
equation to start with let this be ten look at this carefully let concentration
of c l o minus the initial concentration i mean   that means what you are starting with is zero point one mole that is mole
 so per liter
let the concentration of b r minus   b lesser than that which is two point zero times
ten to the power minus three moles per liter ok
 so you set up the reaction conditions such that
these are the concentrations of the hyperchloride   and bromide that you are

starting with now what
you soon realize what you soon realize is that this concentration of color minus is much much greater than the
concentration of b or minus   in other words what we say is in other words
what we say is that i write in the next page that c l o minus is in excess ok c l minus is in
excess over b r minus now how much excess   again that is a very valid point that is a
next logical question you are going to ask   you know what is the difference or what is
the factor in terms of the concentration   difference
 so let us do that
 so then
the consideration of c l o minus over b r minus is equal to if you remember
 so this was zero point one   mole per liter and this was two point
zero times ten to the power minus three   mole meter inverse ok you do the math is very easy
you will see that this ratio comes to fifty fifty what does it say what it means is see it said
that c l minus is in excess that means c l minus is in fifty fifty fold excess
ok c l minus is 50 fold in excess then b r minus
now let us see what is the effect of this
 so that   means you let the reaction run and what you do
is you plot kinetic profiles
 so lets now look at   the kinetic profiles of the two reactants the
two reactants being hyperchloride and bromide
 so let us look at the one
first for the hypochlorite
 so for the hypochloride
 so what we
do is we say that if this is the profile of the reaction ok and suppose there are
some time points out here right this is where   i have taken the points ok so
this is for the hypochloride   and what i have on the y axis is the concentration
the molar concentration of hypochlorite   ok thats what i have on the y axis now the way
i am labeling my y axis and at least in terms   of you know the numbers is the following that
i say it is 100 times 10 to the power minus 3   okay
 so that is 100 times 10 to the
minus 3 which is point one and here i say   ninety eight times ten to the power minus three
so what has happened is you are seeing that as the   reaction progresses between that of hyperchloride
and bromide this is the change i have for the   hyperchloride and say this observation time
is t n and say this observation time is   t n ok now let us draw the similar
kinetic profile but this time for bromide ok again what we have done is we will be
taking the same experimental points right   on the y axis what we have is the concentration
of bromide in moles per liter remember now here   what i do is i will put in the

concentration
values
so for example bromide i start from two point zero say ten to the power minus three and see where i end at
so this out
here say is about this one zero point five minus three ok now what is the significance
of the thing or the profile that we have just drawn for the two
so the top one belongs to
that of the hyper chlorine the bottom one belongs to that of the bromide
so what are you seeing here
as we saw that the chloride the hypochlorite was 50 fold excess
so this is what you see out here
again it is hundred times the minus three and two times to the minus three
so its fifty four
excess the starting concentration hypochlorite is fifty four excess than that of bromide now
you look at bromide
so from two it has come to a very low value right say we are observing it for the same time axis t n rather same time point
so when we are talking about the consumption of
the reactants we stick to this time point t n ok and at t n at this t n we are looking at how
much of bromide has been consumed and how much of hyperchloride has been consumed right
so what
do we see we see for the bromide we see for the bromide it has come down from two to very close
to zero right but look at for the hyperchloride what has happened for the hyperchloride for the
same time point it has come down from hundred to a value which is very close to hundred right
just below ninety eight ok we have been consuming the same amount of both because it is related by
the stoichiometry of the equation but something much more important has to be understood out here
what is that what you will see out here is that the bromide in this case being of limited quantity
it is almost fully consumed
so i can write the bromide ion is almost fully consumed however the hypochloride
was in such large excess that we can write the clo minus is being consumed to a very little extent and that is
so we can say then
that this concentration of c l o minus with respect to that of bromide that means with
respect to the concentration of bromide can be treated to be constant and this is what the subsequent parts of
a discussion would rely on or would be dependent upon that is when i have one reactant which
is many times excess in this case fifty fold excess then the other reactant
so in this case
hyper chloride is fifty times excess than that of bromide then the bromide is almost fully

consumed but the hyperchloride is consumed to very little extent
so the change is minimal
change for hyper chloride and hence we can say or consider the hyperchloride ion concentration to
be constant throughout the course of the reaction because the change for hyperchloride has been
very small but the change for bromide has been huge and this is something we always have to
think about when we talk about these reactions where one reactant is far more in excess than
the other reactant clo minus or the concentration this was in excess has essentially remained constant constant throughout the reaction has essentially remained constant throughout the reaction now
if that is
so then what we say is that if the clo minus has remained
constant then i can say that ok i can treat c l o minus even at t n to be almost close or equal to that of its initial
value why because it is not change at all
so there is no problem if i make this assumption
that the concentration hypochlorite having not changed that much at all then is then
essentially equal to the concentration i started with which is the initial concentration
right
so again based on the kinetic profiles what i have seen out here is that this bromide
concentration has changed significantly by the concentration of hypochlorite c l o minus has almost not changed at all very very little
change and under these conditions we can say that the concentration of color minus has
essentially remain constant to the extent that we go ahead and make the approximation
that the concentration of column minus is approximately equal to the initial concentration
we started with its not a bad approximation at all now how does this help us
so you will soon
realize how it helps us
so let us go back to this rate expression
so the rate expression we
started with was this r is equal to k c l o minus alpha b or minus beta
so this was ten now
this can be replaced as r is equal to k minus alpha
so i am replacing c l of minus x 0 minus 0
because it is not changed at all it is approximate to be equal to the initial concentration started
with b or minus beta
so let this be 11 right now once we have made this approximation once we have
changed c l o minus concentration to c l minus 0 that means initial concentration then
you see what happens is this term this term is effectively a constant isn't it because c l minus initial concentration
constant c l minus has not changed at all approximation is because the change is

so little that is equal to the initial   concentration it started with times k which
is the rate constant which is obviously a   constant
 so i can rewrite i can rewrite this
red equation or this red expression like this
 so remember i am having this i can rewrite
it as r is equal to r is equal to k prime   b r minus bar beta
 so let this be 12
where where k prime is equal to what k   times concentration of c l o minus zero result
per alpha this is
 so number thirteen
 so this is the key point
 so you can see that you started
with two reactants that means several reactants   in case more than one two to start with this
was a difficult proposition because we say   that we have to disentangle the effects
of these two as the rate depends upon both
 so how did we disentangle we said that ok one
of the ways of doing this is to take c l o minus   one of the reactors which in this case is excess
so fifty four excess or fifty fold 50 times rather   54 xs or 50 times more than that of br minus
once it took that what we saw is that the cll   minus concentration did not change at all very
little change hence in the rate law which was the   proposed weight law we said that ok then this k
this ah the c l o minus concentration is replaced   by c l o minus zero right it's replaced by this
zero raised to its corresponding order alpha fine   having done that because this is a constant
and this k is also constant we can immediately   replace this by another constant which is k
prime this is k prime and this what is this   k prime equal to k prime is equal to k times
the consideration minus initial concentration   raised to the power alpha and in this original
equation what we have is r is equal to k prime   times v minus to the power beta
so what we done this is this essentially becomes what this essentially
becomes a equation or rate equation depending only on the concentration of p or
minus because the c l or minus is held   constant right and having said this having said
this having said the fact that this the rate   is now dependent only on b r minus
because this one was in huge excess   we say that the kinetic contribution now
mark these words having said this we say that kinetic contribution of this br
minus concentration has been isolated ok the kinetic contribution of minus has been
isolated
 so that means i have kept the other   reactant in
 so huge excess that now the reaction
rate is depending on b r minus exclusively and   that is how you have isolated

the effect of b
r minus out that you have disentangled you have   separated the effect of b r minus on the reaction
rate from that of hypochlorite c and minus   right and this is been done how by keeping clo
minus in large excess
 so only because you have   kept the other react in large axis have you been able to manage or have you been able to isolate   the reaction such that it depends only on one of
the reactants which in this case is b or minus   because the other reactant was in huge excess
this form of red expression is something which   depends only on the single reactant as you can see
right no other reactant this is what you wanted   anyway because you wanted to disentangle the
effects i keep telling that separate out the   effects and by doing this you have been able
to do exactly what your aim was or what you   started out with the goal that you had started
out with right ok
 so moving forward on this   experimentally now i am let us move forward and say that ok since r is equal to k times b r minus   power beta
 so this was thirteen now
experimentally we will do the experiment say that we observe beta is equal to one right then we say that r   is equal to k
 so this will be
prime sorry k prime b r minus minus sorry b r minus raise to the power one or r is equal to k prime b r minus ok
 so once we have introduced this isolation method
we went ahead and did the experiment right and   found out that beta is equal to one right once we
found out that beta is equal to one we rewrite our   rate expression which is having k prime remember
k prime is equal to k times concentration of c l   o minus the initial consideration raised to the
power alpha times this b r minus where beta now   is known to be one
 so under these conditions
what we say is that this equation we say is a pseudo order equation right is a pseudo order equation   and in this case because beta
is equal to one we say its a pseudo first order equation ok we say
its a pseudo first order equation why   in this case beta is equal to one now
hopefully you will understand where   what i aimed or what i you know try to do
by introducing the isolation method was   i introduced to you this pseudo order equations or
pseudo first order kinetics and how was this done   it was done by keeping one of the concentrations
of the reactants of or the concentration of one   of the reactants in huge excess over the other one
so that this one did not change hence the reactant   or the reaction rate was uniquely dependent or
exclusively depend upon the other reactor which in   this case is v r minus
 so from two reactants you
have kept one reactant in huge excess
 so that it   the rate is depending upon the other reactant

exclusively this is called the method of isolation and likewise what you have done is
it is another pseudo right it is a not exactly a first order but it is a pseudo first order
rate constant or a pseudo first order equation where you have obtained this by keeping the
concentration the other one in huge excess now there are many reactions there are many reactions
which follow these pseudo order kinetics or pseudo in this case first order kinetics and they are
very common for example the acid hydrolysis of ester right ethyl acetate is ah an example of this what i will do is ah ok
so you know before ah
finishing this up ah next class i will take just a couple of examples
so you know this was one
way of doing it right now you can understand that ok how do we know how it depends on the hyper
chloride
so in that case what we say is a fine now i have taken hypochlorite in large axis now
the next point is i will take the concentration of bromide bromide in much excess over that
of hydrochloride say again 50 times more
so under those conditions what will
happen is r can be written as k minus alpha then b r minus beta but because b or minus is enlarged axis i can say that this is equal to b or minus zero the initial concentration
so then r is equal to k times b r minus zero beta c l o minus alpha
so this is now a constant this
is our constant i can name it as k double prime hence r would be k double prime c l o
minus alpha ok and let this p 15 ok
so now you read an experiment before where the hyper
chord was in excess you got the order with respect to bromide in this case again through
the experiment where the bromide is in huge excess but you get the hypochlorite the reaction
rate depending upon the hyperchloride exclusively again you will find in this case that alpha
is equal to one right once you find alpha is equal to one then you immediately realize that
the rate is equal to k times minus b r minus and this is what you were aiming for because the
two reactants were reacting together they were affecting the reactant rate together what you said
was that ok i want to separate them out
so in one case i took one reactant excess let the reaction
it depend upon the other reactant in the second trial what i did was i took the second reactant
now in excess and allowed the first reactant to define or dictate by reaction rate and hence
get my final rate expression ok
so this is called the isolation method and by doing the isolation
method what we have also introduced you to is pseudo order equations or pseudo

in this
case pseudo first order rate equations ok we will do more examples in the next class
and then we will move on from there ok thank you you