welcome everybody to this class this
is a lecture five on chemical kinetics we will start from where we had
left off in the previous class   and if you would remember that in the previous
class we had introduced a concept referred to as   the degree of advancement of
a reaction
and we were monitoring d psi
 so that was   psi is the degree of advancement of
the reaction over time that is dt
 so at the end of the class nearing the end of the
class this is where we had left off what we had started to do this was the
reaction we were looking at   acetaldehyde going to methane and carbon monoxide
then we said we assume ideal gas behavior   assuming ideal gas behavior we write
the initial
number of moles we say that this is the progress   of the reaction the progress
of the reaction being
denoted by the extent of the reaction which is   psi or the degree of
advancement of the reaction
once we are done with that we started writing down   the number of moles of each
and every
species
 so this was the number of moles   of acetaldehyde and zero c h three c h
o or n n naught c has to say h o minus i   why it is minus because we are losing
the reaction
or reactant then n c h four is equal to psi   y again this one is equal to psi
number one
n naught c c h four there was no product to   start with cho was not there and
then because
it is a product you are gaining it as a function   of time it is having a
positive value and the
coefficient is one
 so it is n c h four is equal to   psi and same we are having nco which is
also equal to psi then what we have is initial number of moles the initial
number of moles is n naught c h three c h o is equal to n
naught
 so that is what it is right where zero   or not represents the initial number
of moles
and n naught c h to the c h o essentially is   what n naught c h two c h o means
that this is
the only species that i have i have present at   the start of the reaction now
then how can i
write the total pressure
 so the total pressure   can be written as follows
 so the total pressure
is equal to
 so this is equal to the pressure   from c h three c h o the
pressure being exerted by methane and the pressure being exerted by carbon
oxide
now again remember that we are taking the ideal   gas assumption where ideal gas
means p times v
is equal to n r t where n is the number of moles
 so having done this having done
this what i can do is i can write   p c h three c h o is equal to the number of
moles of acetaldehyde which is n zero minus   psi right into r t by v y
 so this is what we are

doing
 so ideal gas pv is equal to nrt what is n   n n for acetaldehyde is n naught right
 so this is n naught minus   psi because psi is the extent by which the reaction is progressed times r t by   v
 so this is what we have p c h two c h o is equal to n naught minus z times r t over v   likewise we can write the same for p c h four this
is equal to psi r t over v why because psi is the   number of moles of methane and then the same for
carbon monoxide is psi r t over v ok now having   written this now we can go for expression of the
total pressure
 so how do i write that then i can   write remember the total pressure p total is
equal to p c h three c h o plus p c h four plus   p c o right sum of all the components present in
the reaction then we already have expressions for   each of these p c h two c h o p c h four and p c
o we just wrote those down
 so i can write that as n zero minus psi this is the number of moles of
s del d i plus psi the number of moles of methane   plus psi the number of moles of carbon monoxide
times rt over v
 so what did we do out here we   essentially just added all these up p c h t c h o
plus p c h four plus p c o r t by v is a constant   y because temperature is a constant volume
is a constant and hence i can take r t by v   out as a common factor
 so that's what i have done
then p is equal to n zero minus psi plus psi plus   psi times r two over v
 so then i can write p is
equal to n sorry n zero plus psi then r t over v   i can further simplify this by writing n zero
r t over v plus psi r t over v now this is a   significant point or this is a significant step
in the reaction
 so if you would realize this component has n zero times r t over v n zero
is was the initial number of moles
 so remember   see if i write it here n zero was the initial number of moles ok
 so n 0 was the initial number of moles
if that is
 so then i can say that this one is the initial pressure which we can say is p naught
 so the
initial pressure is p naught
 so p naught is   equal to n naught r t over v plus this psi i
t over v
 so p now can be further written as   the p can be further written as that is the
total pressure can be further written as   p is equal to p naught which is the initial
pressure plus psi r t over v now what we do is   we look at it take the differential form of it

you know you know differentiated with respect to t
so the total pressure which is equal
to d p naught over d of t plus d of t psi r t over v if we do that now p naught is a constant right
so i can say p naught is a constant because the initial number
of moles is n naught which is a constant hence this one is equal to zero thus the equation gets
simplified to d p over d of t there is a rate of change of pressure with time is equal to r t over
v r t over v r is a constant t is has been kept constant v is also constant these were the initial
conditions of the reaction d psi over d of t right hence i can further write this one as
so let me write this again on the next page
so what we just had was d p over d of t is equal
to r t by v d psi of d t or d z over d of t right hence i can say that one by v d psi over d of t
is equal to one by r t d p over d of t
so this is what we were aiming for and the problem so
what have we done we have looked at the change in the extent of the reaction
so we have looked
at the change in the extent of the reaction which is d psi over d of t this times one by v v is a
constant is equal to one by r t d pi d p by d t that means that means if i follow the change of
pressure with respect to time that is equivalent that is equivalent to following the change
of the extent of the reaction as a function of time and this one by v times d z over d of
t is what nothing but the rate of the reaction and thus we say that the rate of the reaction can
be monitored by monitoring the change of pressure with respect to time the only thing is there is
there are these constants one by rt because these were kept as constants
so thus this example shows
you how to incorporate or how to you know express the rate of a reaction in terms of the change of
pressure in a gaseous reaction the example being the one we were discussing right now
so hopefully
by doing this exercise or rather an example you would understand the essence of this psi
the degree of advancement of the reaction and the utility of the same in expressing the
rate of the reaction in terms of whatever you want it to be whether it is a concentration
or in case of gaseous reactions whether it is the pressure
so now what we will do is having
established this concept of rate in terms of psi having looked at operational definitions of
rates of reactions in terms of the coefficients and changes what we will now do
is we will now look at something which is much more widely used that
means we are slowly taking a step into the crux of chemical kinetics which is

our kinetic analysis and rate equations
so then i start this section by writing kinetic analysis of experimental data ok and we will soon realize what it means
but in short the significance is that when i am doing an experiment on or related to chemical kinetics i
am following the rate of change of concentration either of reactants or products
as a function of time i generate some plots and what we will see is what do those
plots help us in interpreting in terms of the different definitions of rates which are
out there
so let us look at this one first what we will you know try to discuss out here is something known as average rate something known as average rate
so for example you take this one you take this plot ok
so what i have here is time it can be any unit lets take it seconds
doesnt matter what i have on the y axis is concentration and what i am doing is in this case as an example
i am looking at the change in concentration of the reactant as a function of time right i can also
do it in ah using products but let us stick to change in concentration of the reactant ok so
this is what happens then i will draw a line now just to show you how it changes as a function
of time ok now there is an arbitrary reaction i am taking a very general reaction i am not
naming the reaction as such ok it can be applicable for any general reaction now suppose
we put our experimental points say for example as a point out here right let there be a point
out here let there be a point out here and let there be a point out here
so the line is a smooth
line through some of these experimental points right now it is very similar if i can ah you know
kind of take you back a couple of lectures ago it is very similar to this kinetic reaction
profile that one is also kinetic reaction profile and you can see for these blue
lines which corresponded to the products the reaction between hypochlorite and bromide
giving hyper bromide and chloride how the reactants were changing as a function of time and
this is what i am doing out here too but what are we trying to do or what am i trying to tell you
or what am i trying to emphasize upon
so let this you know correspond to t one let this expandable
point correspond to t two is correspond to t three correspond to t four right
so let
this concentration correspond to c one c two c three and then c four
so what we have done is we
have taken a few exponential points we have labeled them correspond to
the times t one two t three t four and the corresponding concentrations at
those times c one c two c three c four now when we define the average rate when we define

the average rate say we define the average rate between c one and c three so when we take the average rate the average rate is defined as the average rate is defined like this the average rate is equal to say i am taking these two points c 3 and c 1 corresponding to t 3 and t 1.

so c three minus c one over t three minus t one so that is my average rate so if i can write here this is average rate this is equal to c 3 minus c 1 over t 3 minus t 1 i am sure you now realize there is one thing that is missing based on our previous discussions the rate has to be a positive quantity c 3 minus c 1 is negative because c 3 is less than c 1 t 3 minus t 1 is positive because t 3 is greater than t 1 hence this expression is negative because this expression is negative the rate cannot be a negative quantity i have a negative sign out here and again whenever you express the rate in terms of the disappearance of a reactant it is always preceded with a negative sign which signifies a it is a reactant which is disappearing with time and two the rate is a positive quantity and that is why this negative sign has to be there but this is not so useful in very few cases very very few cases you would actually see the average rate being used extensively its not extensively used anyway this one we can write as minus delta concentration over delta t so delta means a finite change in concentration over t a finite change in time that means over the time interval t three minus t one so this is the definition of your average rate and as i said this is not what is regularly used or is that useful what is really useful for us is to know or is to ask if i take any time point if i take any time point on this curve say t 1 say t 2 say t 3 say t 4 say any other time point will i be able to get to get the rate at that specific time corresponding to a certain concentration right what does this bring us to this brings us to the concept of instantaneous rate and that is the one we normally use throughout so let us go and take a quick look at what instantaneous rate is all about so we are talking about instantaneous rate again let us look at a similar curve right where the reactant concentration is decreasing as a function of time so let me have a curve like this ok again same tables this is concentration of reactant i say the reactant is represented as r right this is time in this direction increasing right and my reaction

profile of the kinetic reaction profile goes like this ok and
remember what we are discussing out here is something referred to as instantaneous
rate now suppose these are certain time points or experimental points now
suppose i want to know suppose i want to know
that at this instant that means at this instant at this time point what is the rate what is the
rate at this time point say which corresponds to say in this case it is t one say
so what
would i do is i would draw a tangent if i can draw it properly let me use a different
color i would draw a tangent right at this point
so let me just change this
so i draw a tangent right at that point i
draw a tangent and then what i do is i take the slope of the tangent
so that means i have drawn a tangent
right at t one right at t one once i have drawn the tangent right at t one this is what my the
change in concentration of r which is d of r and along this axis i have can write the change in t
which is d t
so the way this instantaneous rate is different from the average rate is this when
i say instantaneous rate what i am meaning is you know going back to this average rate
definition where c 3 minus c 1 over t 3 minus t 1 when i am talking about instantaneous state what
i mean is i am meaning that c 3 minus c 1 tends to 0 t 3 minus t one tends to zero
so this
is based on the expression we had out here
so there is very small difference between ct
and c one essentially that means i am taking the rate at a specific point hence the rate or the
instantaneous rate is defined as d c over d of t
so based on this based on this what i can write is
so based on this exercise what i can write is then the rate
so i can write r instantaneous which
is the instantaneous rate is equal to is equal to d of r over d of t right with a negative sign
before that again the negative sign has to be there because r being the reactant the rate has
to be a positive one
so what is the instantaneous rate giving you or what is the instantaneous rate all about the instantaneous rate is the slope of the tangent the slope of the tangent drawn at that point that point means the point where you want to find the instantaneous written ok
so i will write it
so that becomes clear so
then the way we characterize instantaneous rate or try to find instantaneous rate is by drawing a tangent at that instant or that time point which in our discussion was t one

so t one is number one and then once i have
drawn a proper tangent
so tangent has to be done properly right once i have drawn a
proper tangent then what i do is i take the slope of the tangent
so these two things i need to do
to find the instantaneous rate ok
so if this is a rate or if you are
looking at the rate in terms of the reactant concentration it would be minus d of
r over d of t if you are looking at the rate in terms of the product concentrations it would
be d of p over d of t
so that means for products similarly i draw i will
draw a tangent at that point and my r instantaneous would be d of p
over d of t this time p here is product p here is product
so this is a very crucial
difference between the instantaneous rate and the average rate
so the average rate is taken
over a longest time interval a long change in concentration over the time interval and it
is not of that much use thats why its not used there often the instant dna state is typically the
one which is used throughout and that is what we saw or what we looked at how it is defined
based on this you can understand that i can have instantly address rates at typically many
points
so i can have see if you if you want this point now right if you want this point what
you do is you draw a tangent at this point right now my tangent was not
drawn properly or if you want to at this point you draw again a tangent at this point ok
so if you want it
here then you draw a tangent at this point
so wherever at that instant you want
the rate you draw the tangent at that point and then do the exercise that means take
the slope of the tangent for example here you take the slope
so from here to here what are we looking at we are looking at
a change in the reactant concentration from here to here what are we looking at we are
looking at a change in time why because this is the y axis the y axis is telling you about
the concentration of the reactant this is parallel to the x axis it is telling you about the
time that is elapsed or rather the time interval d t in this case infinitesimal time interval right
and that is the definition of instantaneous rate and this instantaneous is the one
which is used almost all the time ok there is one more aspect that we have
so we have talked about average rate we have
talked about instantaneous rate a very important rate that comes in a type of rate
is referred to as initial rate that is initial rate of reaction initial rate of

reaction and how do we do that see what does initial rate of reaction mean initial rate of reaction means that exactly at the start of the reaction i need my rate that is the
moment the reaction is started i need to calculate the rate of the reaction see unless and until my
direction has started i cannot calculate any rate or what i am saying by initial rate is that if
i have to calculate my initial rate i have to be very very close to the start of the reaction i
have to let the reaction start otherwise i cannot calculate any rate anyway but once the reaction
starts i immediately calculate reaction rate
so at the very initial point at the very first few points
so then if i have to depict it pictorially or using a kinetic reaction profile same thing if i have
this for a reactant this is time this is concentration right if this is my initial time
point remember this is zero
so this is my initial time point i have to find the initial reaction rate
so what i do is what i do is i draw let me use this pen this is clearer i draw tangent
at this point i draw a tangent at this point this tangent this tangent what does
it give you it gives you the initial reaction rate from the slope of this line and the way this tangent
is drawn is it is drawn right at the initial point of the reaction now this was is you know
this was in terms of the reactant that's why you see decreasing as a function of time i can do
exactly the same thing in terms of the product
so for example if i have not done it before for
the other cases but just to complete the story again this is time this is you know concentration of product this is concentration of product and i say the product reaction profile goes something like this ok
so look at the initial time point
now
so the initial time point is this this is time 0 and if i have to look or if i have to get the initial rate the initial rate or the tangent has to be drawn right at
this point and hence again this is my initial reaction there is an initial reaction rate from product right
so as usual i can get my initial
reaction rate from the reactant and i can get the initial reaction rate from product two points worth remembering one when i you know
later what i will try to do is i will give you some idea of ah you know how people would measure
rates and
so on and there is a method referred to as method of initial rates
so method of initial
rates actually takes this into consideration right you look at the initial rate and then you get
kinetics and other informations about the reaction whichever you are doing at

the time those things will discuss in due course but there are two important points if you are doing an experiment so from the experimental point of view from experimental point of view there are two key points when you do this initial rate calculation one it is preferred it is preferred to do the initial rate calculation based on product appearance so that means if you are given an option if someone asks you during calculation of the initial rate which would i rather choose should i go and use the reactant profile or should i go and use the product kinetic reaction profile your answer would be the product why this is something we need to understand see when we are considering the initial rate of reaction that is very logical you will see see when you are considering the initial rate of the reaction in terms of the reactant loss or reactant disappearance see at this point at this point you have a huge amount of reactant right and then very close to that initial time point you are trying to get a measure of how much of reactant has been lost but do realize that if you do not have a very sensitive technique or very sensitive analytical technique because you are very close to your initial time point right the difference in between the two concentrations that means the slope you take the difference between the two concentrations experimentally would be very small because this difference would be very small if the analytical technique is not sensitive enough then you might not get much accuracy i repeat when you do this initial weight calculation so please remember this when you do this initial weight calculation or experiment you would rather do this in terms of the product appearance as opposed to the reactant disappearance why when you consider the reactant the reactant is present say there is no product at all you are doing the initial rate which is very close to the starting point of the reaction you have lost only a little bit of the reactance say depending upon the reaction obviously and because there was a lot of reactant to start with and you have lost a little bit if your technique is not sensitive enough to figure out the difference then you will not be able to get a proper reaction rate that means your reaction rate calculation would not be that accurate however think about the product so that means the rate in the reaction if this is the initial rate you get very close to the very close to the starting point which it should be which you should be which is my next point for the initial rate calculation then the difference between the two concentrations you measure might not be high and if the technique you are using is not a very sensitive analytical technique then the change in concentration you get might not be the accurate one on the other hand think about the product appearance see look at this product appearance when starting at t 0 which is my initial part even before the reaction is started on y axis we have concentration of products i have no product at all right now the moment my reaction is started a little bit of product has come in but because my initial concentration product was zero it becomes much easier for me to measure that change in concentration because i am always comparing with zero where there was nothing and i do this change with respect to zero or blank that means there was no product out there and hence i am in a much better position in terms of accurately telling or determining the product concentration and then the initial reaction rate from the product appearance and that is why the statement was made it is preferred to do the initial rate calculation based on product appearance experimentally and the second point is the second point is this initial rate calculation has to be done very close to the starting point in terms of time of the reaction it is typically you know thats what people say it is ah typically you know within five percent

so understand what i am saying is where would i measure the initial reaction rate which points would i take where would i experimentally measure this is within five percent of the reaction within five percent of the reaction that means the reaction started it goes to hundred percent reaction complete within the first five percent i would have to take my concentrations for my initial rate calculation finally if you would realize from this the slope of this line and the slope of this line that for almost all reactions provided they are not chain reactions again keep this in mind provided these are not chain reactions apart from chain reactions and talking about all other reactions this initial rate the tangent or the slope of the tangent at the initial rate is always the steepest that means the slope is always the maximum that is the line is the steepest

so we can write except accept chain reactions except chain reactions right the initial rate line or tangent if you would prefer to say that will be the one which is the steepest that is having the maximum slope steepest means the one which is going to have the maximum slope and thats why it is the initial rate

so what did we learn from these plots we looked at three different rate definitions one was the average which was delta c over delta t then was the instantaneous by which we meant that you take any time point on that

kinetic reaction profile
if you want to know the reaction at any time point   thats why its called instantaneous rate at that
instant say t1 t2 t3 then what you do is you draw   a tangent at that point draw the tangent properly
once you have drawn the tangent you take the slope   of the tangent and that slope gives you
the instantaneous reaction rate at that   instant that time part corresponding to a certain
concentration the third one is called the initial   reaction rate and by definition the
initial reaction rate corresponds to   that reaction rate which is measured very close
or right at the initial part of the reaction   and as i said one of those two points it is should
be within the five percent of a reaction whether   it is in terms of reactants or products and
obviously it is preferred that instead of reactant   you use the or reactant disappearance you use the
product appearance to define your initial reaction   rate or find your initial reaction rate this
is something which is very important for you to   understand and also take into consideration if you
are looking at a certain experiment and trying to   figure out what the initial rate is this as i was
telling you this method of initial reaction rates   is very important in determining the rate constant
and even the order of a reaction which you will   realize when we do a few examples later now
having talked about the different types of   rates that are present out there our next
approach which i will start off a little bit today   unless a next approach would be to figure
out something known as rate expressions   that means how is this rate related to the
concentration in some way or the other
so lets   think about that for a bit
so what we do now
is we start with this concept of dependence of reaction rate on concentration and pay attention to this
so let me draw again ah kinetic reaction profile for
a reactant ok
so this is again concentration of reactant which
is r ok this is time as usual now let me draw the profile suppose this is a profile now let's see what is happening let us take a
couple of points along this reaction profile
so let us take this point out
here which say corresponds to t one right and i draw i you know i am trying to find the instantaneous rate at this point   take a
so if i try if i am trying to find the
instantaneous rate at this point what i would do   is i would draw a tangent at that point having
said that lets look at another point out here again i need to find out the instantaneous

rate at this time point say which is t two i do that how as before what i will do is i will again draw tangent ok now hopefully you realize what i am getting at another time point say i take this one t three ok again i draw a tangent i take another time point say here corresponds to t four and i draw another tangent let me write these lines as a b c d e f and then g h so there are four time points at the four time points at the four time points i want to know the instantaneous reaction rates so what have i done at all or each of these four time points i have drawn tangents so for time point t one my tangent is a b for time point t two my tangent is c d for time point t three my tangent is e f for time point t four my tangent is g h now immediately realize because the instantaneous rate is nothing so instantaneous rate is what is the slope of the tangent obviously with a negative sign right because this is a reactant we are talking about i am not writing that its obvious what you will understand is if the slopes if you look at the slopes of the lines a b c d e f and g h this is the order of the slope a b the slope of a b is greater than the slope of c d which is greater than the slope of e f and which is greater than the slope of line g h so a b is having the maximum slope so this guy line a b has the maximum slope and this one has the minimum slope i just want to mention that what i mean by the maximum slope when i say maximum slope what i actually mean is its that the magnitude of the slope is the maximum ok again what i mean my maximum slope is the magnitude which is i am talking about the magnitude of the slope is the maximum and so please remember that whenever i refer to the slope as being the maximum slope or the minimum slope it is always the magnitude that i am referring to so this is the one i am always i am always referring to ok so this is something which is very important to keep in mind in terms of the slope or slopes that we are talking about or we are going to talk about in the later classes right you can see how steep this one is less steep this one is lesser less steep at this one and finally this one is the least steep or having the smallest slope what has happened what has happened is as i move from t is equal to zero along the time points t one t two t three and t four i am losing that means reactant is disappearing that means the concentration of the reactant is changing because of the concent because the concentration of the reactant is changing you can see the instantaneous

rate is also changing which is defined by the slope of the tangents is also changing
so that
means the rate is maximum at the time point t one and it is based on the example given out it
is minimum for time point t four the moment you see a picture like this you start thinking
this ok this is why the rate of the reaction is somehow dependent upon the concentration
of the reactant which is remaining i repeat i will stop here by this or you
know making the statement since the slope is changing as a function of my time points and
since the slope is my instantaneous reaction rate that means the rate instantaneous
reaction rate is changing as a function of time what is also changing
as a function of time is your concentration and if you try to merge both these observations what would immediately fall
out is that the rate is some way dependent on the concentration of the reactant that is
remaining in the mixture and maybe this is where all or this is what is the starting point
of the rate expression which is proportional to the constant of the reactant raised to
some power which we will come to know as the order of the reaction we will look at it
in more details in the next lecture thank you you