welcome to ah lecture number ten on chemical
kinetics
 so if you remember last time we had   started discussion on this isolation
method
and then we had talked about this pseudo order   rate equations where one of the
reactants was
being taken in excess and
 so that you know the   rate of the reaction was depending upon the second
reactant and last time i told you that since we   ran out of time we could not
look at some relevant
examples
 so let us look at a couple of examples   for this pseudo first order rate
equation or
pseudo force order expressions or reactions
 so for   example one of the very common examples
is the hydrolysis of ethyl acetate and this is acid catalyzed ok
 so that means you are looking at the reaction
where the hydrolysis of ethyl acetate is happening   and this reaction is being
catalyzed
in the presence of acid or by acid
 so then we can light the reaction down as c h 3
c o o c two h five right this has been catalyzed by h plus ok the acid and what
we getting
is c h three c o o h plus c two h five o h
 so we are looking at the hydrolysis of
ethyl acetate this is this laser acid   ok it is being hydrolyzed in terms of
acid in
solution to cetic acid and ethanol now here r the rate of the equation can be
written as the rate constant k times ethyl acetate and water but see water is in
large excess right
obviously this has been catalyzed by acid
 so acid   is impressive in there
 so water is in large excess
right
 so because water is in large excess then you   will soon realize that this k
which is this itself
is a constant times h2 will be a constant because   h2 essentially being in
large excess will not
change in terms of concentration that much
 so what we can do is we can rewrite this equation
as as we have done before r is equal to k h two o   c h three c o o c two h five
ok now this
based on a previous discussion this is a
 so now then we can write r is equal to k prime
c h three c o o c two h five
 so here you saw   that the water was a large excess
 so the
water concentration was essentially constant   right hence that was absorbed
into this constant
so we get a new constant k prime where like before   k prime is equal to k times
the concentration of
water right and we can say this k prime is the pseudo first order rate constant
it is a first order rate constant because
you can see the order with respect to ethel   acetate is one right

so that was one example where
we looked at the acid catalyzed hydrolysis of  ethyl acetate another example is
very similar
one but for a different compound is is given as  follows lets look at this
reaction right now again
this is an example of pseudo order rate equation
 so here we have this compound c six h five n two
c l its called benzene dizonium chloride ok in  aqueous form plus h two o plus
h two given c six
h five o h equals plus n two gaseous plus h c l  is aqueous ok
 so this is the requisition then this
is the decomposition of benzene dissonant chloride  right in water giving rise
to these products
right this equation is happening at a certain  temperature here also like
before i can write
the r is equal to k times c six h five n two  c l times concentration of water
again because
water is a solvent itself right this reaction is  happening in order hence
again we can write
r is equal to k prime c six h five n two c l right where k prime is equal to k
times
h two o ok is exactly the same as before  for the case of ethyl acetate right
where
again in this case water is in large excess  and this is your pseudo order rate
expression
again this is a case of pseudo first order  rate equation and this would be a
pseudo
first order rate constant ok
 so these are  two examples which corresponded to the isolation
method and then the pseudo order rate equations  now what we will do is if you
remember we
had talked about one more method and the  method was the initial rate method
 so along with
isolation method the second method was the initial rate method
 so what are we doing here again we go
back to the same equation where we have a b going to products p and we have a
possible
rate expression as k times a to the power alpha  for beta what is the initial
rate method say
 so the initial rate method says based
on the definition of this initial rate  what it says is that i am only going to
consider
the rate which is happening at the initial part  of the reaction remember we
are discussing about
the initial rates very very close to the initial  part of the reaction where
the reaction is
starting
 so then i can rewrite my initial rate
 so if the initial rate is given as r zero
then i can write r zero is equal to k times  concentration of a to the power
alpha but this is
not
 so a naught means the initial concentration  of the reactant a and then the
initial constant

reaction b raised to the power beta ok let this be equation number one now what does this initial

rate method say what it says is see again this is   a case where we have multiple reactants right and

hence we will have to disentangle the contribution   of both the reactants we cannot look at them together

 so we have to look at them you know   singly

 so the last case was isolation method what we did was we took one of the reactants in large   excess right and hence the rate only depend upon

the second reactant in this case what we will do   is by definition this being the initial rate

method what we will do is we will devise an   experiment like this the experiment is device like

the fact that ok we do a series of experiments ok what do we do here is we take one of the reactants say take the initial initial concentration of reactant a to be constant in all these experiments which means a naught is a constant ok

 so what are you doing then suppose you are doing three experiments   right you are doing three experiments knowing the

fact that there are two reactants a and b right   we have to decouple the contributions of both

ok separate the contributions of both what we   are doing is we are taking a naught right and we

are saying that ok for all these three experiments   the initial concentration of a which is

given by a naught is kept the same it is kept   or it is it remains a constant right it does

not change right ok once we have that then   let us go back to this red expression right this initial rate expression

 so based on r discussion   then what we can write is again r zero is equal to k a naught alpha b naught beta

 so this was one right

but now a naught is a constant   right because it is not varying i have kept that k is a constant

 so this is another constant hence again i can write r naught is equal to k prime

 so b raised to the power beta zero

 so this initial concentration of b raised

to the power beta whatever the order is   this is true where k prime is equal to k times

concentration of a naught raised to the power   alpha now this might look very similar to the

isolation method but remember in the isolation   method in the isolation method what we had to

keep was we we said that this concentration of   a naught if this it was a naught for the isolation

method this a was it was not a n or it was a and a   was taken in huge excess and because a was taken

in his excess the concentration of that hardly   changed and hence it was taken to be a constant

but in this case we are not saying that we are   not taking a in large excess

instead what we are
taking is let me reemphasize what we are taking is   that we are saying that this initial concentration
of a which is a naught is held constant ok again the initial concentration of a naught is held constant this is the main idea you are not taking
a in excess please this is the difference between   the one we just looked at which was the
isolation method and this initial rate method   in this initial rate rate method by the
mere definition of this initial rate what   we are saying is the initial concentration
of one of the reactants is kept constant in   a series of experiments that we are looking
at may be three four experiments whatever   and the other reactant which in this case is b
the concentration of that is being varied
 so what   will happen is the rate of the reaction would
essentially then depend upon the the variation   in the rates would depend upon the variation in
the concentration of p and not that of a because   a naught is kept constant right ok
 so here
again this k prime ok becomes a pseudo order rate constant ok this k prime again becomes
the pseudo very just exactly the same   as before let us look at an experiment or a
series of experiments as you as i was telling you
 so suppose i am looking looking at this reaction as we are doing last
time sorry this this gives c l minus aqueous plus v r o minus aqueous ok
 so this is the reaction i am looking at
 so this is aqueous and this is just
the reaction sign here we carried out   say three experiments and this is how the table
looks like
 so we have cut out three experiments
 so the table would be something like
this say this is the consideration of   c l o minus ok initial concentration c l o
minus this is the initial concentration of b r minus and say this is the rate r naught ok what happens is suppose the   initial concentration of c o minus
 so this is
all in moles per liter this is also in moles   per liter right and then you know the
r is moles per liter per second inverse
 so then let me just ah complete this table
 so that i can understand it better ok
 so what are we doing here is so
these are the number of experiments
 so these are the number of experiments right so
for experiment number one say for expert number   one
 so this experiment number one right what do
we have this is these are the following entries

so the initial cost of b r minus is at two point
five one ten to the power minus three ok the    initial concentration of c l o minus is three
point two three ten to the power minus three so    for expanded one i have kept these conditions
and then the corresponding rate i get is    three point one nine to the power minus six
ok now let us go to the second experiment
 so for the second experiment this is what i have
what i say is the concentration of hypochlorite    is six point zero seven times ten to the
power minus three the concentration of    bromide initial concentration you see
i am again writing the same value ok    in this case in this case the rate is given by 5.
98 times 10 to the power minus    6 right and whatever the third experiment remember
i had said we will do a series of experiments
 so the third experiment again the initial
concentration of hypochlorite is given by    nine point two five minus three the initial
concentration of bromide is still kept the same right hence here we see
the r zero now has a value of    nine point one four times ten to the power minus
six
 so the main point out here is the following if you look at this column if you look at this
column this column which has the concentrations of    b r minus the initial concentration of b r
minus for each of these friction one two three    the initial concentration has been kept
constant this is what the initial rate method is
 so you are not taking b r minus an excess right
what you are just doing is you are just making    sure that for all the three experiments the
concentration of bear minus has been kept    constant it is not getting varied at all what
is varying what is varying is the concentration    of hyperchloride right you can see it goes from
three point two three ten from the minus three    to six point zero seven times on the minus three
in x one two to nine point two times ten square    minus three based on this variation what you
see that the reaction rate is also varying the    initial rate is also varying right now keep
this in mind we will come back to this again
 so lets move forward and try to analyze
this initial this table
 so remember    r zero based on our definition of the initial
rate from here should be given as you know say k o minus alpha b r minus beta right
 so let this
be let this be equation three does it matter    now because this one
 so this would be
initial rates or initial concentrations    this is kept constant then i can write

r zero
is equal to k times concentration of p r minus   the c l o minus alpha this
again is a constant right because k is a constant b r minus
zero has been taken to be a constant   based on a table the concentration
was never changed
 so we can say that r zero is equal to k prime c l o minus like this before ok
right
 so again k prime in
this case is a pseudo order rate constant we   do not know what the order is
that yet as yet now
having done this go back to our initial you know   discussion in the previous
class we had looked at
this we had looked at the same reaction and we had   come to the conclusion or i
told you
that for this reaction r is given by this expression right
 so this one i told
you before
 so now the thing is yes i know this   you know i did parallel experiments i
did
some other experiments i know that it is   first of all with respect to hyper
chloride and
first with respect to bromide ok now how do i   how do i make sure how do i make
sure that the t
that the data that have been shown in this table   the data that are being shown
in this table is
consistent with this one well not exactly this one   if you go back to see this
if you go back to look
at this r zero when i say r zero is equal to k   prime where k prime already
includes k times
the initial concentration of b r minus then would the data given here would the
data given
here satisfy the value or satisfy this equation   for alpha is equal to one that
means what are we
going to look at what are you going to look at is   based on equation four you
know based
on equation four what we can say is that   k prime or r zero is equal to k prime
c l o minus
for
 so if this was equation four from before   then what we will be having is the
ratio of r zero
over the constant initial consider hyperchloride   alpha is equal to k prime
right is equal to k
prime now if alpha is equal to one if alpha is   equal to one then r zero by c l
o minus will
always be equal to k prime where k prime is a   pseudo order rate constant in
this case if
alpha is equal to it would be pseudo first   order rate constant right
 so what it means is that
i have these three experiments right i have these   two experiments experiments
one two three for
each of these two experiments i know that the   initial quantity of bromide is
fixed the rate
initial rate is varying and the concentration of   clo minus the initial
concentration is varying

which means which means that based on this   for each and every experiment r zero over c l o
minus the initial concentration should be equal to   k prime the same value only under these conditions
we would understand that alpha is equal to   one and hence it is first order with
respect to hypochlorite and then this   is a pseudo first order rate constant now
do we see that actually happening
 so let us   quickly do a few rough calculations say
for experiment sorry say for experiment one ok
 so r zero i will remind you r zero was
given as three point one nine minus six   moles heater per second ok the
concentration of hyperchloride   was given as three point two three
into ten to the power minus three moles per liter right once i have
this what i can do is i can say   let me calculate this r zero by c l o minus zero
what would that be
 so that would be equal to three point one nine ten to the power minus six
moles per liter per second let us write the units
 so that we can see the dimensionally we
are also going in the right direction   over three point two three times ten to
the power minus 3 moles per liter ok this   would be equal to i am writing the value is 9.
88
times ten to the power minus four second inverse   ok
 so this is what this is equal to k prime based on our equation number six
so this equal to k prime and remember   we are going to see whether the table justifies
the fact that alpha has to be equal to one   right that the order with respect to
hyperchloride has to be equal to one   right ok
 so this was expand one
 so let us
go for x one two then
 so the experiment two has this set of values
 so r zero was
given to be five point nine eight   minus six moles per liter per
second the initial consideration of   hypochlorite was six point
zero seven minus three moles   per liter you do the same thing again which is r zero over c l o minus not
 so this is equal to what five point nine eight times
ten to the power minus six   moles per liter per second over six
point zero seven minus three moles   per liter ok
 so now you can see what will happen
is the same units will cancel out and what we will   be left with is this answer where we have nine
point eight five times ten to the power minus four   second inverse again this is equal to k prime
remember the k prime that we had before it was   nine point eight eight times to the minus four
this is nine point eight five times in the minus   four per second inverse
 so they are very close
so they are very close since we have done these   for the two experiments let us

go for the
third one
 so going for the third one experiment three
 so let us write those values down r zero
is nine point one four minus six moles per liter per second then the initial
concentration hypochloride is given as
nine point two five times ten to the minus three moles per liter right then r
zero over
c l o minus you can do it if will come   to nine point eight eight times ten to
the power minus four sorry second inverse this is again equal to k prime
 so what does
this tell you for all the three experiments   for all the two exponents x one
three nine point eight eight times   minus four second inverse exponent two nine
point
eight five ten is the minus four second inverse   expand one nine point eight
eight ten to the
minus four second rows
 so for all the three   experiments right k prime is almost the same
because k prime is almost the same it the table   the data shown in the table
justifies the fact
that alpha is equal to one that means the order   with respect to hypochlorite
is equal to one so
this is extremely important that we understand   what the difference is between
the initial
rate method and this ah isolation method
 so the concept is the same in isolation
method you take one in large excess
 so that the reaction rate does not depend upon it
because the concentration of that does not change   almost change the top in
initial rate what are you
doing you are saying that ok i am not taking the   react in large excess what i
am only
doing is i am looking at the initial rate   and i am making sure that for all
the series of
experiments i do the initial rate of that reactant   is being kept constant the
moment the initiator of
that reaction is is kept constant i know that my   reaction rate the variation
on the reaction
rate will only depend then on the other reactant   whose concentration is also
being varied initial
concentration and from there i pick up the order   in this case whereas we found
its
alpha is equal to one
 so this was   you know what we learned from here was that if
we have a multiple ah you know reactant equation   then how do you try to figure
out the contribution
of each and every reactant
 so if you have two   is a bare minimum right just more than
one then what you do is you make sure that   by somehow your design experiment
that one
reactant is kept constant either by keeping   it in large excess or by making
sure that the
initial rate is kept constant
 so that it does   not contribute that much to the variation in the

reaction rate as we do a series of experiments
 so if the reaction rate then varies it only has to
vary because it depends upon the second reactant   and that is how we figure out how the second
reactant is contributing to the reaction rate   now once we have done it for the second
reactant we do it for the other one which i was   right now you know keeping constant now
i just switch it or reverse the method
 so whatever thing i was keeping constant before
i allow this one to vary and whatever i was   getting varied before i allow that one to be
constant
 so in isolation method the two forms   which is sorry i mean in in this case i have two
ah ways isolation method and the initial rate   method
 so the isolation method i keep something
in large excess in the initial method what i do   is in for the series of experiments i say that ok
please keep the initial rate to be the same right   and that is how we follow up and get the final
rate expression okay
 so hopefully given you know   this ah table i have been able to make it clear
to you what the difference is between these two   ways these two methods it is extremely important
for you to keep in mind that in one case   you are keeping this reactant in excess and the
other case you are just keeping the initial rate   or initial concentration to be the same but not
in excess ok
 so now we come to a very important   topic in chemical kinetics or a section in
chemical kinetics which we say is the temperature dependence of reaction rates
if you remember our discussions all throughout   right what we said was that if we have to figure
out the rate expression for any given reaction   we have to keep the temperature the same why did
we say that we said that because reaction rates depend upon temperature
 so reaction rates depend upon temperature and generally generally increase in
temperature in general leads to increase to increase
in the rate of a reaction   ok
 so increase in temperature in general
is to increase in the rate of a reaction let us consider the following reaction
 so here i have say i have these reactants c h three
i plus c two h five o minus giving c two h five o c h three plus i minus ok
 so this reaction is taking place in ethanol   right now you do a series of experiments what are
you doing is you are varying the temperature for   this reaction and you looking at the reaction
rate ok
 so this is what you get now you plot
 so you are varying the temperature and

what you are doing is you are plotting this   as a function of temperature
 so let this be temperature ok
 so here on the y axis what
i am plotting is imploding k the unit being liters mole
inverse second inverse ok in this case the temperature is in kelvin just
so i never mentioned this before but just to   make the point to be very
rigorous when you
are drawing graphs on graphs you know you never   you cannot you you can only
put in numbers right
no units or anything
 so what you have to do is   whatever you are putting on the axis you have to
make sure these are pure numbers how do you make   sure these are few numbers
 so if you are given
the value of k right and what is told to you   that this is a second order rate
equation where
r i can ah well i can write this here here for   this r is equal to k times the
concentration
of methyloid and the concentration of ethoxide ok
 so this is a second order rate equation right
because there is second order equation which is   ah one with respect to both
the
reactants i know that this is the   unit for k the rate constant
 so what i am doing
is because i can only plot numbers on graphs   i take k it is in a certain unit
and i divide
that by the unit
 so i get the pure number   right but anyway but the point
is when i draw this graph
 so just let me put this in a box
 so that
its evident what i am doing here   and i draw the plot
 so the
plot goes something like this ok
 so say this corresponds to two eight to zero say this
corresponds to a temperature of 300 again   you see the temperature has been
taken in kelvin
okay
 so that's why because the temperature is   in kelvin again we can plot only
numbers on axis
so i have taken the temperature and divided by k   hence i get a pure number
right
so i have taken the unit out   anyway the point is see if i have these
ah you know these experimental points and what i have drawn is i have drawn a
smooth
line through this experimental data points so   i have taken the rate constant
the secondary rate
constant and have calculated the rate constant   and plotted it as a function of
temperature right
at this say 280 kelvin this is the rate constant   the next temperature this is
the rate constant the
next temperature this is the rate constant at 300   kelvin which is the last
temperature i looked
at this is the rate constant you can see the   way it is increasing it is a very
steep or rapid

growth ok one thing you have to be careful is that    the temperature always has to be expressed in the
kelvin scale not in the centigrade or any other    scales now once you have this dependence
then you are going to look for an expression    which would tell you how the rate is going to
vary right
 so in that case what we all know is the expression that is generally used is k which is the rate constant is equal
to a e to the power minus e a by r t or i can write k is equal to a
exponential minus e a over r t b both are exactly the same expressions
right only in the first case the e has been    replaced by exponential thats it
ok this equation is known as the rnas equation ok this equation is known as the ordinance equation
what is a
 so there are few very important things    in this equation we look at those as we go on
to the ah you know with the discussion on ah    the temperature dependence of the reaction rates
but to start with look at this a and look at this    e a
 so what is a
 so based on this k is equal
to a
 so or minus e a over r t right
 so a is often referred to as the pre exponential factor ok or it is also referred
to as the frequency factor ok or you can also see as arrhenius
factor ok that is a whatever e a e a is referred to as the activation energy or
we can say arrhenius activation energy it goes without saying that k is
the rate constant right is the rate constant right t obvious is temperature and what about r
r is the gas constant the universal gas constant    ok
 so what does this expression tell you what
the expression tells you is it tells you the    variation of k along with temperature
so there is an exponential dependence on    the inverse of temperature right k being the rate
constant what is r r is the universal gas constant    a is referred to as the pre exponential factor
or frequency factor or the arrhenius factor    what is e a is called the activation
energy or also referred to as the rnas    activation energy because this is the
arrhenius equation we are talking about    you know when chemical kinetics was being
developed in the very early stages say between    eighteen fifty to nineteen ten
a lot of work was being done to understand to understand the temperature
dependence ok a lot of work was done to understand the
temperature dependency almost during when you    know this chemical kinetics was getting more
and more developed advanced and people were    bringing in theories and so
forth about chemical kinetics    now during this time there is a
very important quotation in 1904 by ostwald by oswald what did roswell say oswald said see
a lot of you know theories a lot of ah being put    forward for this temperature

dependence a lot of
discussions were given at the time
 so oswald said temperature dependence the temperature dependence of reaction
rates is one of the one of the darkest chapters one of the darkest chapters in
chemical mechanics ok
 so this is very important in 1904   when you know discussions were on in full
swing
about how the reaction is depend upon temperature   also made this statement
saying the temperature
dependence of reaction rates is one of the darkest   chapters in chemical
mechanics which means
that not much light was being thrown upon   this aspect that is how the rate of
a reaction
varies as a function of temperature ok now i showed you this rnas equation where
k
is equal to a e to the minus e a by r t let us try to see how this came into
existence
 so what happened was vantov started with this expression in a very
well known book office
 so vantov said sorry started with this expression
 so what was
the expression
 so the expression was that over del t at constant pressure is equal to del u
naught over r t square
so let this be equation two
 so what you looking at is you are looking at a
partial derivative that means the dependence of   this equivalent constant k c
the natural log of
that ah temperature
 so del l in case your del   t at constant pressure is equal to del u naught
over r t square where k c what is k c k c is the concentration equilibrium
constant right and what about del u naught del u naught is the standard internal
energy change standard internal energy change ok   now let us go back to this
equivalent constant k
c this is the concentration equivalent constant   lets start with this you know
lets just
write down this ah equation or reaction the reaction is a plus b in equilibrium
with its products p
plus q and what you are having is   you are having two rate constants
one is a rate constant for the   forward reaction k one one is the rate
constant
for the backward direction k minus one ok
 so a   and b are the reactants p and q are the products
k one is a rate constant for the forward reaction   k minus one is rate constant
for the
backward reaction it is given that rate constant for the forward reaction
or sorry rate for the forward reaction   i can write rate forward is equal to k
one a b rate for the backward reaction is k minus one p q
 so this is given to you now at equilibrium
what are you what is going to happen   at equilibrium both these rates are
going
to be equal ok
 so let us do that then at equilibrium r forward is equal to r backward hence it
goes without saying i

can write k one a b is equal to k minus one   is consideration of p concentration of q

so if

this says three then i can rearrange and write   that concentration of p over concentration of q

over concentration of a over concentration of b   is equal to now see from this reaction if i write

so a plus b going to p plus q if i write this if i write this expression then this is equal to k c right and this should be equal

to what you see from here from 3   if i bring this on this side i will be having $k_1$ over k minus one ok

so this is   four

so where we are saying that k c is

the concentration equivalent constant   concentration equivalent constant means that

the a b p q these are being expressed in their   say molar concentrations right thats why its

k c c being concentration and this is equal to   k one over k minus one

so what is $k_1$ $k_1$

is the rate constant for the forward reaction   and k minus one is a rate constant for the

backward reaction ok very simple now remember   we had this vantoff's equation which was i will

remove the partial derivative right now k c over   d t is equal to delta over r t squared

so this was equation two for me i have k sorry k c is equal to k one over k minus one this was from equation four

so what i will do is i take this equation

four and put it here

so i will be having using four in two we can have this k c is being replaced by d   natural log k one over k

minus one by d t is equal to r t square right

so once we have this what

we do is we write it separately and say that $d \ln k_1$ over d of t minus $d \ln k_{-1}$ over

d of t is equal to ta u naught over r t square   let this be equation five now from here from

here what i can do is because i have written   this because i have written this what i can

do is i can go forward and write that ok $d \ln k_1$ by d t is equal to $e_1$ over r t square

right d k minus one over d of t is equal to   e minus one over r t square let this be six sp seven if i write this if i write this

then i should be having where delta   u naught is equal to immediately understand

is $e_1$ e minus one plus v eight ok

so these are the two

energies $e_1$ and e minus one   the difference between this gives you the change

in internal energy the standard internal energy if i express this del u naught as you know e

one and e minus one $e_1$ minus e minus one   then this one would be equal to this this one will be equal to this   and just i'll end this class by leaving this

equation with you if i look at both of these   equations if i write the general form saying that

$\frac{d \ln k}{dt}$ is equal to $\frac{e}{rt^2}$   this is the general form and if i integrate

it if i integrate it what i get is natural log of k is equal to natural log of k is equal to constant minus $\frac{e}{rt}$ from where i can say that a k is equal to a minus $\frac{e}{rt}$   this was my arrhenius equation right and somehow moving from vantov's expression of this expression right relating the change   in the equilibrium constant as a function of temperature to the internal energy change   the standard energy change we have been able to reach this expression that now what is we know   as the arrhenius red expression for the or the rnas equation for the temperature difference of   reaction rates ok
 so this is how if you are thinking that how this expression came over   this is how it came over but it is surprising that it came from vantov's equation i have not   yet told you where arenas's importance has come in this i will discuss in the next class ok thank you you