

hello everybody welcome to the 4th lecture  
in this discussion on chemical kinetics just a brief recap actually a very  
quick recap  
you know what we did last class was we were we started looking at kinetic  
reaction profiles  
right and this was the reaction profile we were looking at this was an example  
where the  
reactants were hypochlorite and bromide and the products were hyper bromide  
and chloride  
so very simple reaction the stoichiometry is one for each reactant and each  
product and then  
what we were saying was that the if you look at the blue lines the blue lines  
are belonging to  
those of the reactants what are we plotting here we are plotting concentration  
versus time right  
here time being in seconds and because the blue lines correspond to the  
reactants and since with  
the progress of the reaction the reactants are going to be decreasing that  
means used up the  
products are going to be formed hence you see that the blue lines the  
concentration if you go along  
the blue line the concentration is decreasing ok as a function of time the  
reverse happens  
for the products why because for the products here these are being formed as  
the reactants are  
being used up and hence the products according to the green line or along the  
green line they  
are increasing as a function of time then we started asking the question as to  
how fast is  
this happening can we have a quantitative estimate of the same right  
so how can we have that or how  
did we write that last time  
so if you remember the rate of reaction can be  
either expressed in terms of rate of disappearance of reactance or it can be  
expressed  
as rate of appearance of products  
so you can either do it in terms of the reactants  
which are decreasing as a function of time or you can do it in terms of  
products which are  
increasing as a function of time right because it is the rate of disappearance  
we  
also discussed this last time  
so for reactants if you are expressing the rate of  
reaction in terms of the reactants and in this case the reactants being  
hypochlorite  
and bromide we can express them as  
so this i will just cancel what i meant was the rate of reaction  
you can express them like this the change of the reactant hypochlorite over a  
defined time interval with a negative sign or the change of the concentration of  
bromide over  
a time interval with the change in sign then we also said that suppose my  
delta hypochlorite which  
is this one the delta hypochlorite corresponds to say  $c_1$  and  $c_3$  that  
means  $c_3 - c_1$

one and the  $\Delta t$  I am talking here  $\Delta t$  the  $\Delta t$  corresponds to  $t_3 - t_1$   
 so what  
 you will see is if I express it like this again  $c_3 - c_1$  then  $t_3 - t_1$   
 one ok the first one is a negative quantity that means the numerator is a  
 negative quantity  
 the denominator is a positive quantity and we get a negative value out here  
 because  
 this is negative because this is negative the rate cannot be negative  
 so you have  
 a negative sign out here this negative and this negative cancels out and  
 finally you have a  
 positive value for the rate of the reaction now this is extremely important  
 that you  
 understand for any reactant this is always maintained if you are expressing  
 the rate of the  
 reaction in terms of products right  
 so that means again if I expressing the rate of reaction  
 in terms of products I can express them as this  $\Delta t$  right and if you take  
 the same intervals  
 for example suppose you take  $t_1 - t_3$  for hyper bromide or chloride then  
 $t_3 - t_1$   
 is obviously positive because time is increasing and again if you consider  
 this concentration  
 and this consideration this concentration is higher than that  
 so this is positive over positive  
 which gives you a positive quantity  
 so in terms of products it is always a positive quantity  
 right ok  
 so now let's start with a reaction  
 so let's consider a very general  
 reaction right a very general reaction let's see how we can represent that so  
 general reaction goes like this right a small a which is the stoichiometric  
 coefficient  
 of this chemical species a small b the small b is the stoichiometric  
 coefficient of the reactant  
 b plus other reactants giving you this reaction  
 so on  
 so this is a very general  
 representation of a reaction  
 so what a and b c and  
 so on are the reactants right then small a small a small b small c  
 these are the corresponding stoichiometric coefficients similarly p q and if I  
 write  
 r out there these are products and in the same way small p the  
 small q the small r these are stoichiometric coefficients of the products the  
 point I am trying to make out here is this let the stoichiometric coefficients  
 be  
 represented as something referred to as  $\nu$  ok new spelled as  $\nu$   $\nu$  if the  
 general symbol of the stoichiometric coefficient is given  
 as  $\nu$  then then what we can write is and this is extremely important that  
 we follow and we understand that for reactants or reactant species  
 this  $\nu$  is a negative quantity for products  $\nu$  is a positive quantity ok

so that means  
if you go back to this if you go back to this equation then if i am writing  
 $\nu$  for a  
so if i am writing  $\nu$  for a then it would be minus a if i am writing  $\nu$  for b  
it would be  
minus b on the other hand if i am writing  $\nu$  for p it would be sorry it would  
be plus p if i  
am writing  $\nu$  for q it would be plus q and  
so on  
so that means that means as i have  
written it here for reactants the stoichiometric coefficient is  
considered  
to be negative for products the stoichiometric coefficient is considered to be  
positive right now  
why did we do this exercise you will soon realize let us go back to our very  
general reaction and  
let us take a shortened form of that reaction  
so let us write the reaction again  
so the  
reaction again is can be written like this a plus b giving us the product p plus  
the product q  
so this is the reaction we are looking at ok now again as defined a and b are  
the reactants  
p and q are the products small a small b are the corresponding stoichiometric  
coefficients  
of the reactants and small p small q are the corresponding stoichiometric  
coefficients of  
the products good now what we will do is we will bring in one more term or  
parameter  
that is something referred to as the degree of advancement of a reaction now it  
is very similar  
to something which you have known from other topics in chemistry which is the  
degree of dissociation here we see there is a degree of advancement this  
degree of  
advancement is given by the symbol  $\psi$  ok the degree of advancement is given by  
the  
symbol  $\psi$   
so this tells you by how much the reaction has progressed or advanced as a  
function  
of time right now what we can do is we can write a certain expression which i  
say that  
 $n_i - \nu_i \psi$  just tell you what these mean is equal to  $n_i$  not or zero plus  $\nu_i z$  ok  
so if z is the degree of advancement of the  
reaction and let this be equation one if z is the degree of advancement of the  
reaction you know  
what i can write is the  $n_i$  what is  $n_i$  it is the number of moles of the  
chemical species i  
so that specific chemical species  
so i will  
write in detail later but just to make the point or make the connection  
so if if this i was  
referring to a then this would be  $n_a$   
so it is then  $n_a$  means the number of moles of a or  $n_i$  is  
the number of moles of the reactant or the product represented by that i this

is a b being the reactants or p q being the products now what about you know  $n_i$  naught so this  $n_i$  naught is very significant so this  $n_i$  not or zero is the number of moles of the chemical species i then  $\psi$  is equal to zero so is the number of moles of chemical species i when the degree of advancement as i said the degree of advancement i write it again the degree of advancement of the reaction is zero you go back to this equation so  $n_i$  is equal to  $n_i^0$  plus  $\nu_i$  times  $\psi$  if  $\psi$  is equal to zero as i was telling you if  $\psi$  is equal to zero then  $n_i$  is equal to  $n_i^0$  so what does this mean this means that this is the initial concentration the initial number of moles here i am referring to the number of moles i have not yet brought in the volume but is which will convert it to the concentration units so the initial number of moles is at that point where the  $\psi$  is zero that means the reaction has not advanced at all so this is your initial condition ok again what is  $\nu_i$  by this time you know the  $\nu_i$  is the corresponding stoichiometric coefficient ok so now what we have done is we have taken this equation and we have tried to define each and every term in this equation where  $n_i$  is the number of moles of the chemical species i right then  $n_i$  naught what is  $n_i$  naught or  $n_i^0$  is that number of moles of the species when  $\psi$  is equal to zero that means the degree of advancement of the reaction is zero that means the reaction has not progressed at all and whatever  $\nu_i$  as you just figured out in our previous discussion right a few minutes ago it is the corresponding stoichiometric coefficient whether we are talking about the reaction or whether we are talking about a product right now as defined by kinetics right what this kinetic kinetics means you are looking at the change as a function of time right that is what kinetics is so what we will do now is we will go back to equation one so let me write that again we will go back to equation one which is  $n_i = n_i^0 + \nu_i \psi$  so this was our equation one right now this is our equation one because it is a change with respect to time what we do is we differentiate this equation with respect to time so differentiate one with respect to time because that's what kinetic is we want to follow something as a function of time that means how it changes with respect to time

so then this equation becomes  $\frac{dn_i}{dt}$  is equal to  $\frac{dn_i}{dt}$  zero over  $\frac{d}{dt}$  plus  $\frac{d\nu_i \psi}{dt}$  now pay attention

so what have you done you have

done what you have done is you have taken one and you have differentiate each and every

term of that equation with respect to  $t$  okay let this be equation two

so some simplifications

can be done straight away look at this term this term is equal to zero why is it equal

to zero it is equal to zero because you know differentiation of a constant with respect

to time in this case with respect to time will obviously be zero right because it does not

change there is no change with respect to time

so what is  $n_i$  naught

so  $n_i$  naught as based on

our definition is the initial number of moles which is a constant right

so  $n_i$  naught

is the number of moles where  $\psi$  was zero

so  $n_i$  naught essentially is the number of moles

$i$  started with ok

so again  $i$  define because  $n_i$  naught is a constant which as defined was

the initial number of moles hence  $\frac{dn_i}{dt}$  is equal to zero

so this is  $\frac{dn_i}{dt}$  zero of

$\frac{d}{dt}$  is equal to zero

so that means the initial concentration of the initial number of moles in this case of that particular reactant or product is known to you is known to you

when when  $\psi$  is equal to zero that means when the reaction is not yet progressed at all and because

this is a constant because you know it then the differentiation of this with respect to

time is zero ok the next point is if you look at this factor now or this term over  $\frac{d}{dt}$  this can be written as  $\nu_i \frac{d\psi}{dt}$

why can  $i$  write that the reason  $i$  can write this is because

$\nu_i$  is a constant right what is  $\nu_i$  this is a constant why is it a constant this is

my stoichiometric coefficient of that species  $i$

so then simplifying this whatever we have done we

put this back in equation two and see what we get

so then  $i$  have this  $\frac{dn_i}{dt}$

is equal to  $\nu_i \frac{d\psi}{dt}$  or  $i$  can write it like this  $\frac{d\psi}{dt}$  is equal to one by  $\nu_i \frac{dn_i}{dt}$

so if  $i$  give this say equation number three this is a very important step is a very

important step you will realize that this term this term  $\frac{d\psi}{dt}$

what does it say it is the rate of advancement of the reaction or we can simply say the rate of the reaction we can simply say the rate of the

reaction right

so you already have a term which gives you the rate of the reaction and what is that it is the  $v$  it is the way or the differentiation of a degree of small

advancement with respect to time that is  $\frac{dz}{dt}$  that is the rate of the reaction or the

rate of advancement of the reaction of the rate of progress of the reaction  
 does not matter which way you define it now that is equal to what that is equal to 1  
 by  $\nu_i$  where  $\nu_i$  is the stoichiometric coefficient times  $d n_i$  over  $d t$  and  
 what does this mean it means that  $d n_i$  over  $d t$  represents what the change in the number of  
 moles of species  $i$  over time this times the inverse of the stoichiometric coefficient which is  
 one by  $\nu_i$  is equal to the degree of advancement of the reaction it is very similar it is  
 very similar to something you must have seen in any discussion chemical kinetics or something we are  
 going to discuss down the line but what you have to understand is one more thing if you go back  
 to this equation when I am writing this  $n_i$  is the number of moles  $n_{i,0}$  is the number of  
 moles at the initial time when  $\psi$  is equal to zero  $\nu_i \psi$  is a constant it is a stoichiometric  
 coefficient hence this  $\psi$  is also the number of moles by which the reaction has advanced  
 so then  $d \psi$  by  $d t$  when we are doing this when we are writing this equation finally when we are writing this  
 equation final equation three everything is in terms of the change in number of moles yes  
 number of moles is proportional to concentration but I have not yet brought in the concentration  
 as yet that means the volume is not yet brought in whatever this reaction is representing  
 is the advancement of the reaction in terms of the number of moles being  
 expressed like this so that means  $d \psi$  by  $d t$  which is the change in the advancement of the  
 reaction is equal to one by  $\nu_i d n_i$  over  $d t$  so this is how you know the very familiar equation you  
 have seen or you see typically being discussed in books on chemical kinetics in  
 any book on chemical kinetics comes about now to elaborate this a little more  
 let us go back to our reaction so if you remember what a reaction was I will write again because we are  
 flipping through pages so we might forget  $b$  giving  $p$  and  $q$  so this was the one we started with then based on equation one we had said  
 that  $n_i$  is equal to  $n_{i,0} + \nu_i \psi$  right this was a equation one now if you  
 remember equation this was our equation now suppose I am doing it for  $i$  where  $i$  is a  
 that means I am taking the reactant  $a$  if I am taking the reactant  $a$  how does this  
 equation change

or you know how do we make this equation more visible to you  
 so then because  $i$  is a  $i$  can write  
 $n$  of  $a$  is equal to  $n$  of  $a_0$  or not  
 so this  $n$  of  $a_0$  means what means the initial number  
 of moles of  $a$  you had at time zero where the reaction had not yet started that  
 means the  
 degree of advancement in the reaction was zero plus  $\nu$  of  $a$  and then  $\psi$  let me  
 go ahead and write this one  
 like this  
 so  $n$  of  $a$  is equal to  $n$  of  $a_0$  not now remember going back to our discussion  
 today in the initial part of the class  $\nu$  of  $a$  this is the stoichiometric  
 coefficient of the  
 reactant  $a$  and  $i$  told you that the stoichiometric coefficient of the reactant  
 $a$  is going to  
 have a negative sign  
 so then  $i$  give minus  $\nu_a$   
 so this being  $a$  with the negative sign the  
 reactant times  $\psi$   
 so then  $i$  if  $i$  differentiate it then  $i$  differentiate it  $\frac{d}{dt}$   
 so this is equal to what  $\nu_a$  over  $\frac{d}{dt}$  minus  $\frac{d}{dt}$  right or  $i$  can write it  
 plus right now then minus  $\nu_a \psi$  ah going forward it should be very clear  
 to you that this is equal to zero and hence this equation cannot be written as  
 $\frac{d}{dt} \nu_a$  over  $\frac{d}{dt}$  is equal to the first term was  
 zero then minus  $\nu_a \psi$  over  $\frac{d}{dt}$  or as you had written again before one by  $a$   
 $\frac{d}{dt} \nu_a$  over  $\frac{d}{dt}$   
 so now what have you done what you have done is or what we have done is  
 that we have expressed this rate of reaction we have expressed this rate of  
 reaction in  
 terms of the change in the number of moles of  $a$  which is reactant  $a$   
 so to carry on with this suppose  $i$  try to express this in terms of  
 the reactant  $b$  see when  $i$  say now let  $i$  be  $b$  the reactant  $b$  then obviously  $i$   
 have  $\nu_b$   
 which is the number of moles of  $b$  is equal to  $\nu_b$  naught that the initial  
 number  
 of moles of  $b$   $i$  had present plus  $\nu_b$  the stoichiometric coefficient  
 associated with  
 the reactant  $b$  then the corresponding  $z$  again  $\nu_b$  is negative that means  
 $\nu_b$  is  $\nu_b$  naught minus  $\nu_b \psi$   $i$  differentiate with respect to time  $\frac{d}{dt} \nu_b$  over  
 $\frac{d}{dt}$  is equal to  
 $\frac{d}{dt} \nu_b$  naught over  $\frac{d}{dt}$  plus and once  $i$  have done this  
 realize that this one is again zero and  $i$  have  $\frac{d}{dt} \nu_b$  over  $\frac{d}{dt}$  is equal  
 to minus  $\nu_b \psi$  over  $\frac{d}{dt}$  or  $i$  can write  $\frac{d}{dt} z$  over  $\frac{d}{dt}$  is equal to  
 minus one by  $b$   
 $\frac{d}{dt} \nu_b$  over  $\frac{d}{dt}$   
 so which is very similar to what we had done here  $i$  did not write the rest  
 so  
 from here  $i$  can write  $\frac{d}{dt} \nu_a$  over  $\frac{d}{dt}$  is equal to minus  $\nu_a \psi$  over  $\frac{d}{dt}$   
 right if you look at  
 these two if you look at these two here you can see what  $i$  have done here  $\psi$  by  $\frac{d}{dt}$  is equal to  
 minus one by  $b$   $\frac{d}{dt} \nu_b$  over  $\frac{d}{dt}$  right here also you can write  $\psi$  by  $\frac{d}{dt}$  is  
 equal to minus  
 one by  $a$   $\frac{d}{dt} \nu_a$  over  $\frac{d}{dt}$

so let me write here

so let me write this one here

then i can write likewise that  $\frac{d[\text{psi}]}{dt}$  is equal to minus one by a  $\frac{d[\text{n}]}{dt}$

over  $\frac{d[\text{t}]}{dt}$  what is the similarity similarity is this or are these there are similarities in both

cases you have the rate of the reaction  $\frac{d[\text{i}]}{dt}$  the rate of the reaction is being expressed

either in terms of the reactant a the reactant b right which is  $\frac{d[\text{n}]}{dt}$  or  $\frac{d[\text{n}]}{dt}$

t that means the change in the number of moles of reactant a or reactant b is a function of time

what are these associated with on the right hand side these are associated with the corresponding

the inverse of their corresponding stoichiometric coefficients

so for a it is  $\frac{1}{a}$  for b it is

$\frac{1}{b}$  not only that go back to our discussion in the previous class or with the initial

part of this class where we were saying that the rate of the reaction in terms of reactants

are always associated with a negative quantity isn't it and you see this negative is coming

out where does this negative come out in this case where we have said negative this negative is

coming out from the fact that your stoichiometric coefficient of the reactant by definition is

negative and hence you get that corresponding rates of reactions both in terms of the reactant

a or in terms of reactant b

so obviously it goes without saying that if i now go to the product side a similar thing would come about

so lets now again say for the same reaction

let me write the reaction again giving p plus q with the corresponding stoichiometric coefficients let i be now p ok

so that means now i represents the product

p if i represent the product p then i can write  $n_p$  is equal to  $n_p$  zero plus  $\nu_p$  i or  $\nu_p$  i

would write  $\nu_p$  then  $\psi$  ok we go ahead and simplify it a little further so  $n_p$

is equal  $n_p$  naught now we say plus p then  $\psi$

so this is where you know the

difference between that of a reactor and that of a product

so in case of the reactant the

stoichiometric coefficient had a negative quantity was or was a negative quantity had a negative sign

but in case of the product because we are getting the product you are producing the product right

as the reaction goes by the product is coming into existence its concentration is increasing

so the stoichiometric coefficient of the product typically is given a positive value it is com

associated with the positive sign hence you can differentiate it again  $\frac{d[\text{p}]}{dt}$  is equal to

$\frac{d[\text{n}]}{dt}$  zero over  $\frac{d[\text{t}]}{dt}$  plus  $\frac{d[\text{t}]}{dt}$  then  $\psi$  again this is equal to zero

right because  $n_p$  not  
 being the initial number of moles of  $p$  the product  $p$  is a constant you know  
 that  
 so we can write  $\frac{dn_p}{dt}$  is equal to  $p \frac{d\xi}{dt}$  therefore I can write  $\frac{d\xi}{dt}$   
 is equal to  $\frac{1}{p} \frac{dn_p}{dt}$  right  
 so see what we have  
 so this is what we had for the reactant  $b$  this is what we had for the  
 reactant  $a$   
 so that means  $\frac{d\xi}{dt}$  the rate of the reaction was given by  $-\frac{1}{a} \frac{dn_a}{dt}$   
 ok in terms of  $b$  the reactant  $b \frac{dz}{dt}$  was given by  $-\frac{1}{b} \frac{dn_b}{dt}$   
 in terms of the product however  $\frac{d\xi}{dt}$  is given by  
 $\frac{1}{p} \frac{dn_p}{dt}$  a positive sign  $\frac{dn_p}{dt}$  right hence extending this  
 so it is left as an exercise  
 for you to show that  $\frac{dz}{dt}$  is equal to  $\frac{1}{q} \frac{dn_q}{dt}$  I can  
 write this straight  
 away that  $\frac{d\xi}{dt}$  can be expressed how  $-\frac{1}{a} \frac{dn_a}{dt}$   
 this is equal to  
 $-\frac{1}{b} \frac{dn_b}{dt}$  this is equal to  $\frac{1}{p} \frac{dn_p}{dt}$   
 and this  
 is equal to  $\frac{1}{q} \frac{dn_q}{dt}$   
 so what we have been able to do through this  
 exercise is we have been able to define the rate of the reaction which is  $\frac{d\xi}{dt}$  that  
 means the rate of advancement of the reaction that is what your reaction  
 kinetics is or  
 defined as is defined in terms of what here in terms of the rate of  
 disappearance of the  
 products  $a$  and  $b$  and also the rate of appearance of the products  $p$  and  $q$  these  
 being associated  
 with the corresponding stoichiometric coefficients and the stoichiometric  
 coefficients are  
 also associated with the respective signs what are those for the reactant  
 species the  
 stoichiometric coefficients come with negative signs for the product species  
 the stoichiometric  
 coefficients come with positive signs right this is extremely important for  
 you to keep in  
 mind never forget this that the stoichiometric coefficient  $i$  repeat the  
 stoichiometric  
 coefficient associated with the reactant is a negative number that means is  
 associated with  
 negative sign while the stoichiometric coefficient for the product species is  
 associated with  
 the positive sign again just to clarify what I said just now the  
 stoichiometric  
 coefficient the stoichiometric coefficient is always positive ok is always  
 positive only when it is for the reactant we preceded that means we put a  
 negative sign before the stoichiometric coefficient if it  
 is product we put a positive sign before the stoichiometric coefficient

and this obviously is understandable based on a discussion why because the reactant we are losing as a function of time so we put a negative sign before the stoichiometric coefficient to represent the fact that it is decreasing as a function of time and the product we put a positive sign to say or to represent that this species or product is coming into existent existence rather that means growing as a function of time hence again as a clarification please remember the stoichiometric coefficient is always positive though it is just that when we define a reactant or a product if it is a reactant then we preceded by a negative sign if it is a product then there is a positive sign before the stoichiometric coefficient ok because we want to differentiate between the reactant and the product and we know that any in every reaction the reactant is going to be lost and the product is going to be produced or come into existence ok what we can do is we can just quickly take reaction a specific reaction or chemical reaction or equation and see how this comes out so let us consider this  $2N_2O_5 \rightarrow 4NO_2 + O_2$  ok i am considering what i am considering the decomposition of  $N_2O_5$  based on this reaction  $N_2O_5$  is my reactant species i am looking at the decomposition of that decomposition into what there are two products  $4NO_2 + O_2$  so the products are  $NO_2$  and  $O_2$  and then obviously you have to make sure that the reaction is balanced then what can i do i go back and i look at this definition of  $d\xi/dt$  based on this definition can i write down the degree of advancement of the reaction for this specific equation ok how do i write it so i write then  $d\xi/dt$  is equal to let us consider the reactant first the reactant is  $d(\text{number of moles of } N_2O_5)/dt$  it should be associated with this corresponding stoichiometric coefficient but with the negative sign what is that i write it is minus one by two why because this two is the corresponding stoichiometric coefficient of  $N_2O_5$  and  $N_2O_5$  has to have or has to be associated with a negative quantity so that is what i have out here so this is the only reactant species we have then this is equal to i write the degree of advancement of the reaction or  $d\xi/dt$  in terms of the products this would be  $d(\text{the change in number of moles of } NO_2)/dt$  with respect to time i will be having one by four out here similarly i

can write  $\frac{dn}{dt}$  sorry let me change this again let me write it here clearly  $\frac{dn}{dt}$  what should i write here you see for  $n_2$  the stoichiometric coefficient was four for  $O_2$  to the stoichiometric equation is one

so it is one by one

so i am not writing anything about it because they are essentially one times  $\frac{dn}{dt}$

so going back to this expression again of  $\frac{dz}{dt}$  of  $\frac{df}{dt}$  we have taken a specific reaction we are expressing  $\frac{dz}{dt}$  that means the rate of the reaction in terms of these given species

so for  $n_2$  of five which is reactant it is minus one by two two being the corresponding stoichiometric coefficient into the rate of change of number of moles of  $n_2$   $O_2$  right or  $\frac{dn_2}{dt}$  into  $\frac{d\psi}{dt}$  is obviously a function of time this is equal to one by four remember this is a positive this is a product  $n_2$  it's a positive quantity or positive sign so one by four  $\frac{dn_2}{dt}$  if that is the case if that is the case you can see that we have this is a positive sign out here this one by four  $\frac{dn_2}{dt}$  right and this is equal to the change in the number of moles of oxygen over time what is the stoichiometric coefficient it is one or plus one and hence this is how it comes about

so hopefully you understand that this is how the rates of reactions are written in terms of the change in the number of moles now generally generally what happens is generally what happens is all these things are done under constant volume conditions right all these things are done under constant volume conditions so let us take a specific example or let us go back to our you know equation 1 so you will understand what i am trying to say

so we can say since most of the reactions are done under constant volume conditions then from one which was  $\frac{dn_i}{dt} + \nu_i \frac{d\psi}{dt}$  this was our equation one right and we had written  $\frac{d\psi}{dt}$  is equal to one by  $\nu_i \frac{dn_i}{dt}$  think this was equation three because this is done at constant volume what i can write is by definition it is a constant volume what i can do is i can write like this one by  $v$

so i put one by  $v$  on the left hand side of the equation  $\frac{dz_i}{dt}$  over  $\frac{d\psi}{dt}$  is equal to one by  $v$  because i put in one by  $v$  on this side i have to make sure that i cancel by the same factor on the other side then one by  $\nu_i \frac{dn_i}{dt}$  over  $\frac{d\psi}{dt}$  again

keep in mind that  $v$  which is the volume is constant  $v$  is constant now if this is constant remember this equation what i can do out here is i can take this i can bring  $v$  inside this differential form say i can  $v$  inside

this derivative right and hence i can write  $\frac{d}{dt}$  then in within brackets  $\frac{d}{dt}$   $\psi_i$   $\frac{d}{dt}$  of t see i have brought in  $\frac{1}{V}$  inside or i have gotten one by  $\frac{1}{V}$  inside is equal to one by  $\nu_i$  then  $\frac{d}{dt}$   $n_i$   $\frac{d}{dt}$  of t by doing this simple assumption which is mostly valid for most of the reactions that's what you are doing you are doing reactions at constant volume what about  $n_i$  by  $V$  so see this is the rate of the reaction so again i write  $\frac{d}{dt}$   $\psi_i$  by  $\frac{1}{V}$   $\frac{d}{dt}$  of t is equal to one by  $\nu_i$  the stoichiometric coefficient obviously remains as it is it is a constant right then this can be written as the concentration of the species  $i$  over  $\frac{d}{dt}$  of t so this  $i$  is concentration of species  $i$  now immediately you realize that you have come back or you have been able to reach a point which is very familiar to you and is used universally in chemical kinetics what is it that the rate of the reaction the rate of the reaction which is this the rate of the reaction which is this is given by the change in concentration of that chemical species in this case which is  $i$  over  $\frac{d}{dt}$  of t associated with one by  $\nu_i$  when  $\nu_i$  is a corresponding stoichiometric coefficient and how did we make this conversion from  $n_i$  over  $V$  to consideration of  $i$  its very simple simple is that what is concentration suppose molar concentration is moles over liter what is  $n_i$   $n_i$  is the number of moles and if you have  $V$  in let us you can always do the conversion so you have the corresponding concentration term so this again is an extremely important equation i have to see what is a number i can give just let me check let me give this equation four and remember now this is the rate of reaction so the rate of the reaction is having this expression which is given by the change in concentration of species  $i$  with respect to time weighted by or is associated by the inverse of its of the corresponding stoichiometric coefficient of species  $i$  right good so now what we have done is we have been able to define the rate of the reaction in terms of the change in constant of the reaction or the change in consider of the reactant species or the product species right whatever you can think of using you can feel free to use as a function of time so what i will do is i will ah you know start with the specific ah example let us do an example and see whether you know we have some we if we have a feeling of what we have just discussed right now so what we are going to do is we go we take an example that we are going to focus on so here we have acetaldehyde gaseous giving me methane plus carbon monoxide both in the gaseous states now what is the question or what is the problem the problem is that the rate of this reaction can be followed by measuring can be

followed by measuring the pressure in the system at constant volume and temperature again you are given this reaction  
 acetaldehyde going to methane and carbon monoxide and it said that the rate of this reaction can be followed by measuring the pressure in the system at constant volume and temperature  
 so that means the volume of the vessel and the temperature are being kept constant  
 so how do we proceed with this based on the discussions we had earlier  
 so let me write down the equation again  
 so before writing down let me tell you this that when we are going to go through this problem one assumption we are going to take is the following assume ideal gas behavior  
 assume ideal gas behavior of the gases assume ideal gas behavior of the gases  
 so let me write down the reaction again for the sake of convenience because this is where we will start working with the problem  
 so now having written the reaction down let us think about the initial phase or the starting of the reaction  
 so the initial phase  
 so if i write this one as initial  
 so if i write this one as my initial condition  
 so the initially i have  $n$  moles of acetaldehyde in the reaction vessel but there are no moles of any of the products present  
 so that means the only species i have at the start of the reaction is acetaldehyde  
 of that i have  $n$  moles or  $n$  zero number of moles now with progress of the reaction what will happen is  
 so here we write with reaction progress  
 so with reaction progress i can write  $n - \xi$  moles of acetaldehyde  
 being the extent of reaction of the degree of advancement of the reaction which we just saw then  $\xi$  moles of methane  
 so that means the way the reaction is advancing what we are having we are having  $\xi$  moles of methane as the reaction is progressing  
 $n - \xi$  moles of acetaldehyde minus  $\xi$  moles which is the degree by which the reaction is advanced along with this i have  $\xi$  moles of  $\text{CH}_4$  gas formed and  $\xi$  moles of carbon monoxide formed ok  
 so once we have this you know once we have this lets now write down the number of moles of the individual components  
 so that means  $n - \xi$  moles of  $\text{C}_2\text{H}_4\text{O}$  is equal to  $n - \xi$  moles of  $\text{C}_2\text{H}_4\text{O}$  plus  $\xi$  moles of  $\text{CH}_4$  but remember this being a reactant this being a reactant  
 you are losing acetaldehyde as the reaction is progressing  
 so  $\nu_i$  out here is negative  
 the value of  $\nu_i$  you saw from the previous slide or equation is one that is the coefficient

is one hence what we do now out here is we rewrite it as follows where  $n_{\text{C}_3\text{H}_3\text{O}}$  is equal to  $n_{\text{C}_3\text{H}_3\text{O}}$  minus  $\psi$  right  
 so  $\nu_i$  the value of  $\nu_i$  is one and because you are losing acetaldehyde as a function of time hence its sign is negative so this one is important for the setup of the problem or the way we are going to work with the problem then accordingly i can write for methane so the number of moles of methane which is  $n_{\text{C}_4\text{H}_4}$  like we wrote the number of moles of acetaldehyde  $n_{\text{C}_3\text{H}_3\text{O}}$  the number of moles of methane can be given by  $n_{\text{C}_4\text{H}_4}$  plus  $\nu_i \psi$  ok again if you go back to the reaction the coefficient before  $\text{C}_4\text{H}_4$  is one right same for carbon monoxide the coefficient before carbon monoxide is one hence for methane then this  $\nu_i$  has a value of one and the sign is positive because reaction is progressing and the product is forming so i can write then  $n_{\text{C}_4\text{H}_4}$  is equal to  $n_{\text{C}_4\text{H}_4}$  plus  $\psi$  now also  $n_{\text{C}_4\text{H}_4}$  which is the initial number of moles of  $\text{C}_4\text{H}_4$  if you remember from the previous discussion is zero the same thing is also for carbon monoxide so i can further simplify this by writing that  $n_{\text{C}_4\text{H}_4}$  is equal to what  $\psi$  why because  $n_{\text{C}_4\text{H}_4}$  is equal to zero so this is again this is again another important piece of information that you will need while we walk through the problem so we left with one more component which is one of the products carbon monoxide very similar to that of methane so how do we write that so then for carbon monoxide is what i write  $n_{\text{CO}}$  there is a number of moles of carbon monoxide is equal to  $n_{\text{CO}}$  that is the initial number of moles of carbon oxide present plus  $\nu_i \psi$  is the same thing as that of methane this is equal to zero right  $n_{\text{CO}}$  is equal to zero and  $\nu_i$  is plus one hence i write  $n_{\text{CO}}$  is equal to zero plus  $\psi$  or  $n_{\text{CO}}$  is equal to  $\psi$  so then in a nutshell what have we done we have been able to express the number of moles of the respective components of the reaction be it reactant which is acetaldehyde or b their products which are methane carbon monoxide in terms of the extent of the reaction which is  $\psi$  so we will start from this in the next class you