Environment Engineering: Chemical Processes
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Module No # 02
Lecture No # 08
Rate of Reaction – I

Hello again so welcome back so we have been discussing kinetics in out last class right so we will take you through from there.

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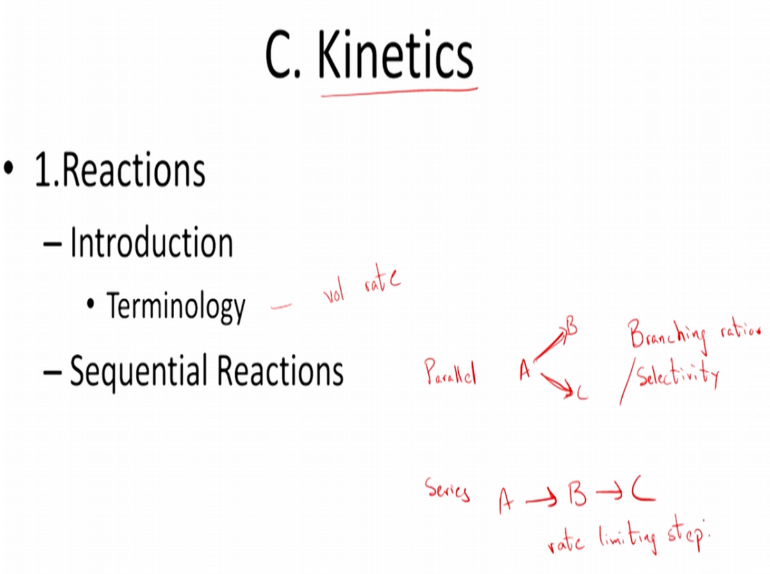

C. Kinetics

- 1.Reactions
  - Introduction
    - Terminology — vol rate
  - Sequential Reactions

Parallel $A \nearrow B$, $A \searrow C$ Branching ratios /Selectivity

Series $A \rightarrow B \rightarrow C$

rate limiting step.

So we have been discussing kinetics or how fast is reaction right and we talked terminology in general we said we are going to talk about volumetric rate and then we started discussing about sequential reactions either parallel or series parallel A goes to B or A goes to C simultaneously and in here are concerned about the branching ratio right or selectivity here I guess.

With respect to A goes to B, A goes to C and in the same case we said we are going to look at A goes to B goes to C and in series we are concerned with what is that the rate limiting step that controls the overall what do we say chemical process here right in this case we are now going to look at few graph I believe.

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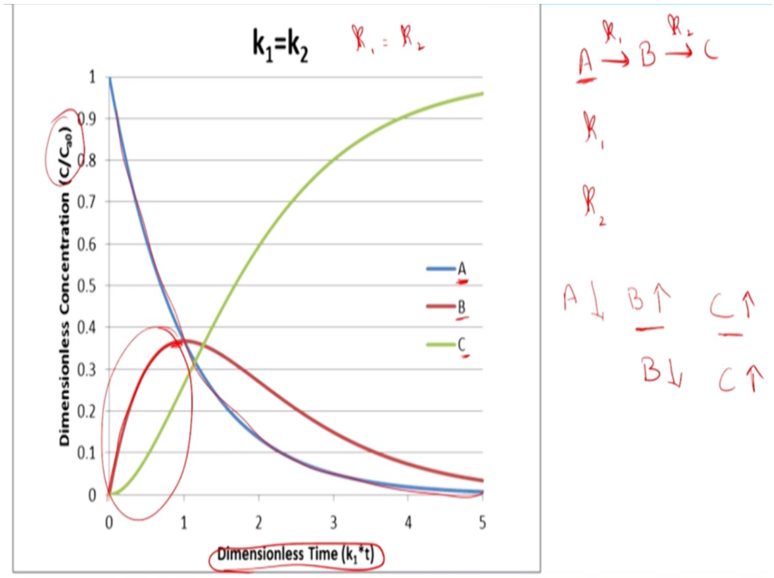

So here we have a particular graph here so the back ground information is I guess this A goes to B, B goes to C rate constant K1 rate constant K2 for the second reaction B going to C right and here in the X axis we have a dimensionless time here that is normalize I guess right not normalize pardon me and we have on the Y axis and dimensionless concentration C / C naught right.

So it gives an idea about changes or concentration of particular what do you say component so here we have A, B and C right and here we have rate constant for example not for example for now think of rate constant as metric to give an idea about how fast or slow the reaction is talk about the greater detail later on right. So this is small K when we see that in this better example K1 = K2 right and obviously what we expect I guess A is decreasing with time right for the reaction I guess what they are.

So A is decreasing with time or this dimensionless time here that is what you see so as A is decreasing as A keeps decreasing you will have B increasing and that is what you see in this particular phase here right so B is increasing at the same time C will also increase whenever B is formed right so that is what you see here and at critical point in time then going to notice that B is going to start decreasing and while C is going to keep increasing.

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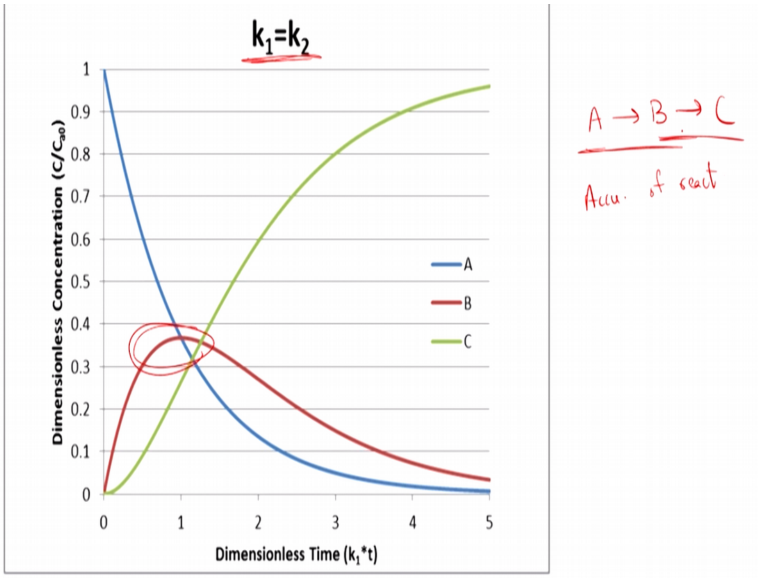

So that is what you see here right so let erase this and start refresh so A keeps decreasing B initially increases to certain point and when it reaches to a certain concentration rate changes again right and that is why you see that there is a net decrease. So initially there is a net increase and then there is a net decrease with respect to C you only see only formation here right.

So that is what you are noticing here and at this point can be any try to highlight which is the rate limiting step here difficult to right in general how do we identify the rate step whenever there is an accumulation of particular reactants let us see accumulation of your reactants. Anyway because you know the kinetics of both the reactions or relatively similar or the rate constants are same. So that is why I guess it is difficult to identify what do we say rate limiting step.

But if you want to I guess just for sake of this theoretical purpose you can say it is accumulating here or B is accumulating so you can call B to C as the rate limiting step but I would not go or go ahead and call back right.

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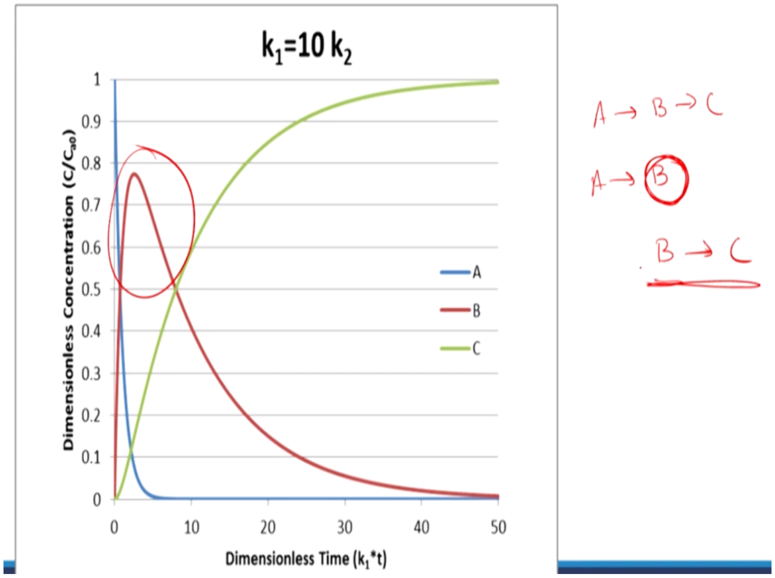

So let us look at another example we will see better what do we say representation of rate limiting step. So here again we have a second example here goes to B goes to C again rate constants 1 and 2 I mean K1 and K2 but the here the issue is that K1 is for greater than or greater than K 2 right. So what you see here you see accumulation or your particular reactants or accumulation of B.

So here we can clearly identify that B to C is your rate limiting step right and for example think of this I am able to go from Roorkee A roorkee I guess very fast to Ghaziabad but at Ghaziabad I have a huge traffic jam or I am hitting traffic and accumulation of traffic and I spend a lot of time there before i can get back to prefer destination which is C I guess so that is what you see here.

So let us look at that once again please so here we have A going to B going to C and A goes to B is much faster than B goes to C so what is that happening I guess right. So you see accumulation of B right that is what you are seeing here and this particular case A goes to B is relatively fast and C is relatively slow. So you have rate limiting step which is B going to C right.

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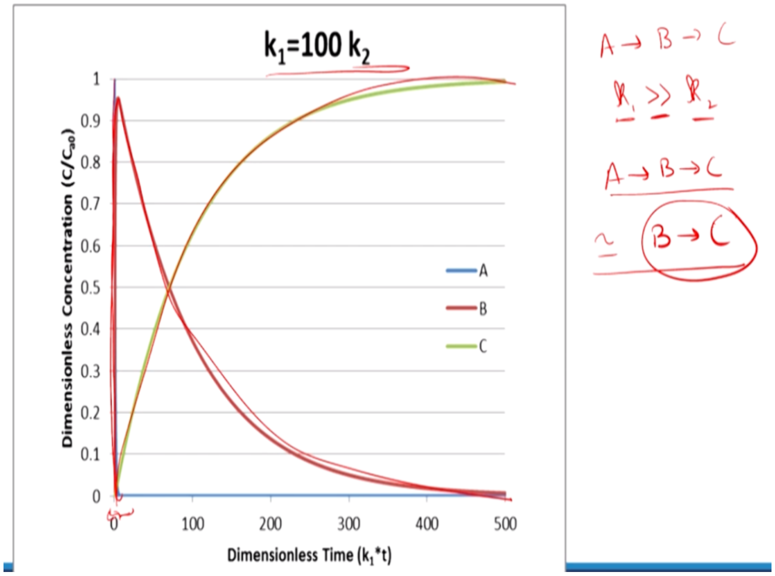

So let us move on to another example here so here we have a same case A geos to B goes to C but here you see that K1 is far greater than K2 right almost 100 times I guess two orders of magnitude higher now right. So what do you see here so a graph by itself be relatively unclear so we are going to look at second graph that what we say looks at this particular region later on.

But try to understand what is happening here so in effect A goes to B goes to C if you look at particular time scale more or less looks like it is similar to just B goes to C right why is that you see instantaneously I guess at least for this time scale all the A is immediately converted to B right and then you have a slow deputation of B to C that is why slowly decreases while the concentration of C slowly increases right.

So in effect A goes to B, B goes to C transforms into just B goes to C and why is the reason what is the reason I guess B to C is the rate limiting step and also K1 is remarkably higher than K2. So to understand the system better let us assume in I guess here the scale is 0 to 500.

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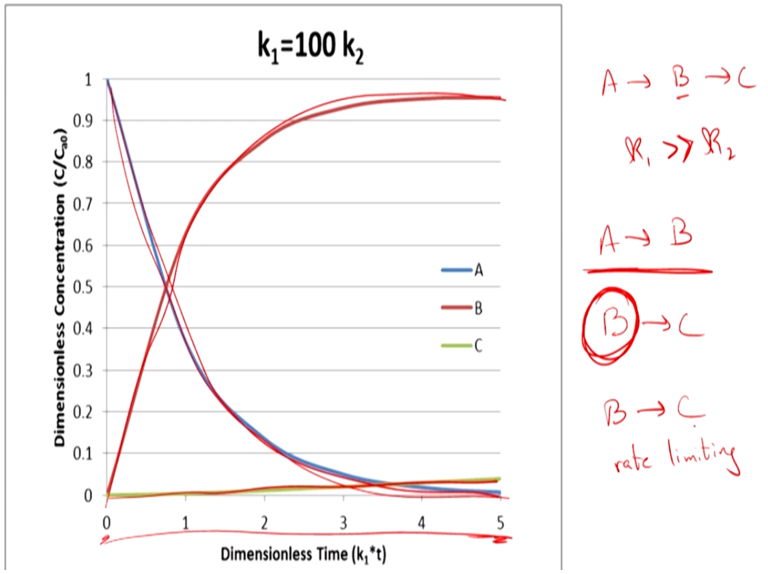

And now we are going to look at the scale from 0 to 5 for the same example as we looked at earlier A goes to B goes to C K1 is far greater than K2 right that is what we have K at the rate constant right and what do we see here now I guess. So we see that with this particular truncated time scale we see now how A is remarkably degraded very fast right and kinetics of deputation of here remarkably fast yes and at the same time B is remarkably fast or the kinetics of formation of B or far we are describing this process right.

But B going to C is very slow and that is why it is very negligible here right so what is why what happens B ends up accumulating and so thus B going to C is your rate limiting step right. So hopefully that is clear.

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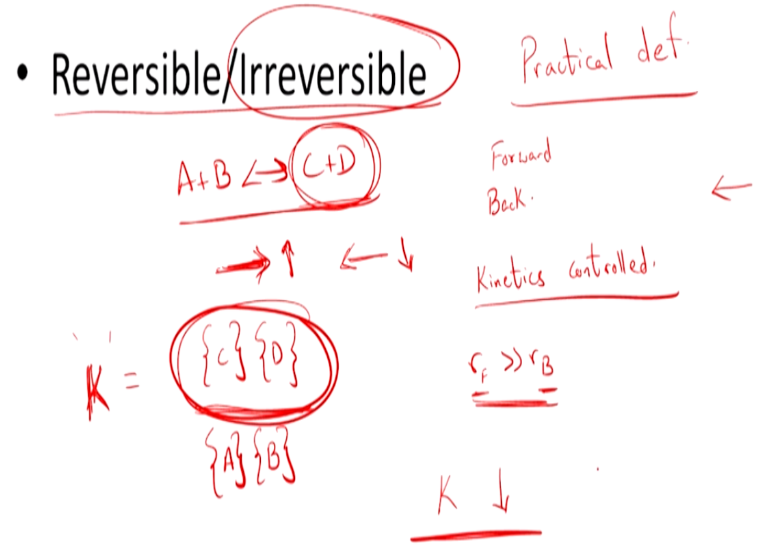

- Reversible/Irreversible

So we will move on to the next set of examples I have so usual case people come across reversible and irreversible reaction but keep in mind these are only practical definitions their only practical definitions. So let us try to understand what they are let us say so for example let us A + B can go to C + D so in general theoretically always have a forward and backward reaction right when somebody say the particular reaction is irreversible what is that mean?

It is a practical definition again it because theoretically all the backward reactions are feasible but when somebody says it is irreversible what is it mean that the kinetics of forward reaction is much higher or faster pardon me than the kinetics of the backward reactions right kinetics of the forward reaction is much higher than the kinetics of the backward reaction right. So in effect we see that people think that it is an reversible reaction but again keep in mind that is a practical definition only.

So it I guess no issue of equilibrium here it is mostly kinetic control not mostly it is always kinetic control it is kinetically control right. So let us look at example of what is this A + B going to C + D I guess what is the equilibrium constant? This is the capital K here equilibrium constant we talked about in the previous classes capital K and what is that equal to I guess equity of C stoichiometric coefficient of all one we are going to not look at into stock activity of D / activity of A into activity of B.

So more or less activity of B products in the numerator activity of the reactants in the denominator right. So this is what we have so when let us say you know the rate of the forward reaction is far greater than forward reaction what would is that mean? So it means that C and D are going to be at remarkably higher what do we say concentration so again these are reactions right.

So again we look at branching activity more or less we no need to go that into greater detail say again here when somebody says that this particular system is irreversible what is it mean now. It means that numerator remarkably high why is that because rate of forward reaction is far greater than the rate of the backward reaction. So everything A as B react to go to C and D accumulate but simultaneously C and D you know going back to reacting to form A and B is very slow right.

So thus you only see accumulation of C and D so that is what you see in that case for irreversible reaction what would you expect equilibrium constant value in general will be relatively low right.

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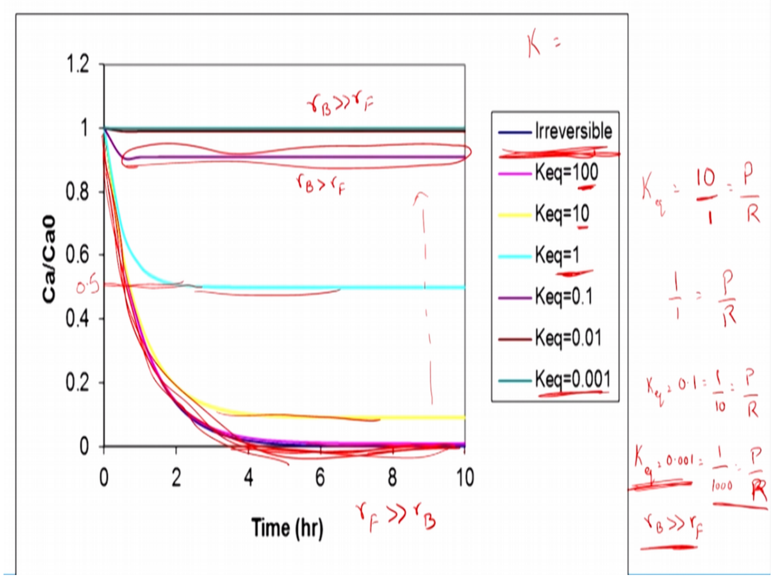

So let us look at what we have here so I believe we have this particular case here right so let us look at this graph here right an equilibrium constant let us say K equilibrium right and what it we have here let us from bottom down. So first step I guess this violet cultured here which we are calling as irreversible right and what do we see here I guess pardon me I guess that is my mistake.

Obviously here the numerator is IK is not going to be low K is going to be high right minor error in what is spoke earlier. So we were clear about that when the rate of forward reaction is greater than rate of backward reaction the numerator is going to be little higher right and you would see that thus the numerator is obviously higher that would mean that equilibrium constant is going to be high.

So coming back to our example so that is what you see here at high whenever we called irreversible what is happening here i guess say everything is being transformed here right. CA is being transformed entirely here right and that is what you see here at a slightly low equilibrium value still more or less the same when K equilibrium is 10 what is K equilibrium = 10 let us say right it still means there are 10 / 1.

So again products by reactant still there are products by reactants ratio is more or less 10 is to 1 right that is what it means here and that is the yellow line here I guess and the next case is K equilibrium = 1 so 1 / 1 and that is why you see it is more or less here 0.5 I guess right CA / CA naught is near 0.5 right.

And as we keep going down what is happening I guess the equilibrium is shifting and when it is point 1 what is K equilibrium = 0.1 may = 1 / 10 so there are more reactants rare than the products lefts so the backward reaction is actually faster than the forward reaction. So the rate of the forward reaction is faster than the rate of the forward reaction that is what you see here and as we keep going up I guess ok going down K equilibrium is 0.001 and what is that equal to? 1/1000 that is the product by reactants layman nomenclature here I guess.

So what is this mean rate of the back ward reaction is much faster than let us say rate of the forward reaction I guess again this is for understanding purpose I guess we are trying to relate equilibrium with kinetics not in good way to do but for your understanding we can look at those aspects right I guess right. So this is what we see here this is irreversible reaction in the forward reaction when rate of forward is far greater than rate of forward reaction.

But as we keep moving up what you see though we see that ultimately we ends up backward reaction is far greater than the forward of greater reaction. So here you have A being completely transformed so initially all the A is converted to products right.

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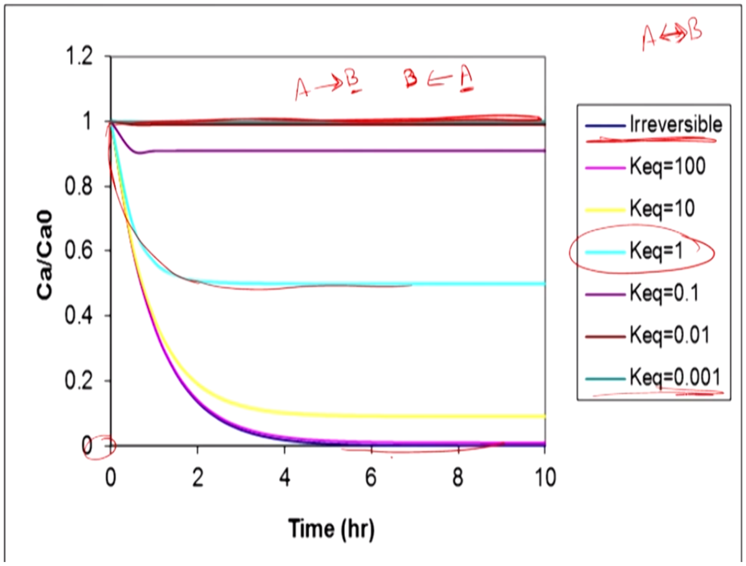

So in this case here you see that in the irreversible case A is completely transformed to the product there is no more A after certain time but let us say in equilibrium = 1 right if this is the case it is going to B let us take all these sets of examples are going to B what do you see I guess. As A goes to B again B is also transformed to B and so on and again the other case A going to B is much slower than B going to A.

So what is this mean any A that transforms to B is immediately again transforms to A again so that is what you see here that is why moral see that concentration of A constant through out that is at the other end of the system anyway we will move on to the next set of slides.

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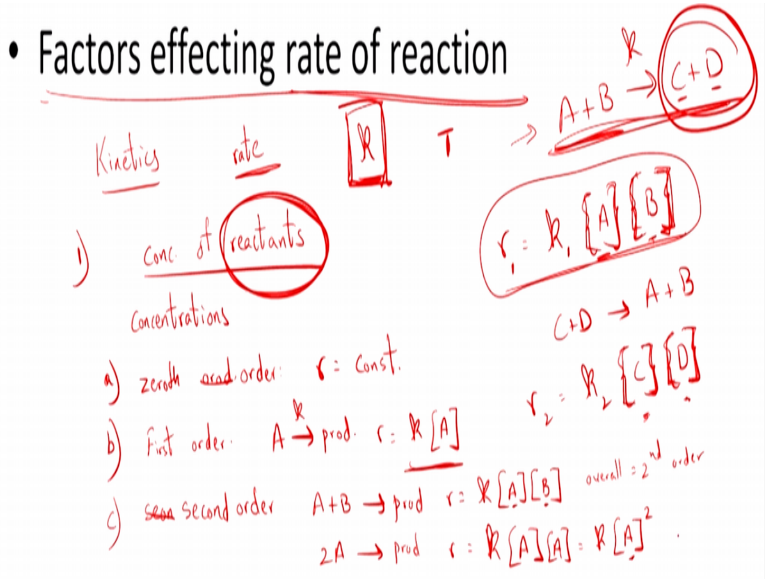

- Factors effecting rate of reaction

$A+B \xrightarrow{k} \boxed{C+D}$

Kinetics rate $\boxed{k}$ T →

1) Conc. of reactants

Concentrations

$r_1 = k_1 \{A\}\{B\}$

$C+D \rightarrow A+B$

a) zeroth ~~orod~~ order $r = const.$

$r_2 = k_2 \{C\}\{D\}$

b) First order $A \xrightarrow{k} prod.$ $r = k[A]$

c) ~~seca~~ Second order $A+B \rightarrow prod$ $r = k[A][B]$ overall = 2nd order

$2A \rightarrow prod$ $r = k[A][A] = k[A]^2$

So here we have factors affecting rate of reaction so kinetics is always inter related to rate of your reaction right so we will look at what it is and what are the factor that are affecting the rate of the reaction. So already we came across one term rate constants obviously it is a constant for a particular temperature anyway. So rate constant that gives us an idea about your particular kinetics rate is certainly going to be dependent on your rate constant.

It is a constant for a particular reaction through A + B going to C + D for this power reaction we will have particular rate constant here let us say right so the major aspect upon which the factor rate of the reaction is concentration of reactants and this is remarkable important though why is that so it only depends on for this reaction as an A + B or A and B going to C and D what is this rate of reaction depend upon it is equal to R = K into activity of A or concentration of A into activity of B.

And this particular reaction we have no what we say variables that look at concentration of the products. So it has in the rate always only depends upon the concentration of the reactants right. So please keep that in mind that the rate always depends upon only the concentration of the reactants. So here it is an concentration right so obviously through if you are looking at the reverse reaction C + D so I will call this R1 C and D reacting together to form A and B.

So for that R2 and this will be K1 and this will be K2 will be obviously equal to K2 into concentration of C or activity of C into activity of D right. I will think that is clear here so in this reaction A and B are the reactions C and D are the products and that is why you see only the variables that talk about or give us an idea about the reactants in this equations and the second equation where C and D react to go to A and B right you have only the activity of A concentration of your pardon me C and D right so that is what we have here.

Anyway you can have concentration here that is not an issue right this should be concentration this should be concentrations it depends upon the concentration of your particular reactants concentrations right. So let us look at the different kinds of reactions that we have so one would be zeroth order usually where we come across this zeroth order right and rate = a constant and only in variable specific cases we usually come across this rate of the reaction are constants right.

And B as a first order and examples A detaining to products and what would be the rate of reaction now rate = K or rate constant for this particular reaction into the concentration of A so at this you see is zeroth order not zeroth order pardon me the first and obviously again we will have the same case second order and we have multiply case I guess A + B going to products or 2A going to products.

So rate would be K times concentration of A into concentration of B and in the second instance is going to be the relevant rate constant into concentration of A into concentration of A what is that translate into I guess that is equal to K into A square both of them are the second order. So the rate is first order with respect to A here first order with respect to B here and overall rate = second order right and here through rate is second order with respect to A and also obviously second order overall right.

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d) $2A + B \rightarrow \quad r = k[A]^2[B]$

$3A \rightarrow \quad \rightarrow r = k[A]^3$

$A + B + C \rightarrow \quad \underline{r = k[A][B][C]}$

r : Conc.

T.

And the same case I believe you will have what we say third order right or 3A goes to products rate would be equal to what now K into concentration of 3A square into B and this will be R = K AQ or A + B + C goes to what now products and R in this case = K into A into B into C. So in this last instance if you are talking about this latter example right so the order of the reaction is first order respect to A first order with respect to B first order with respect to C but third order over all right that is obvious here.

Right in this case or second case it is third order with respect to A or third order overall so that should be relatively over all I guess so we have talked about the rate depends upon the concentration now right and other aspect we need to look at is temperature I believe I have tthat in next slide right.

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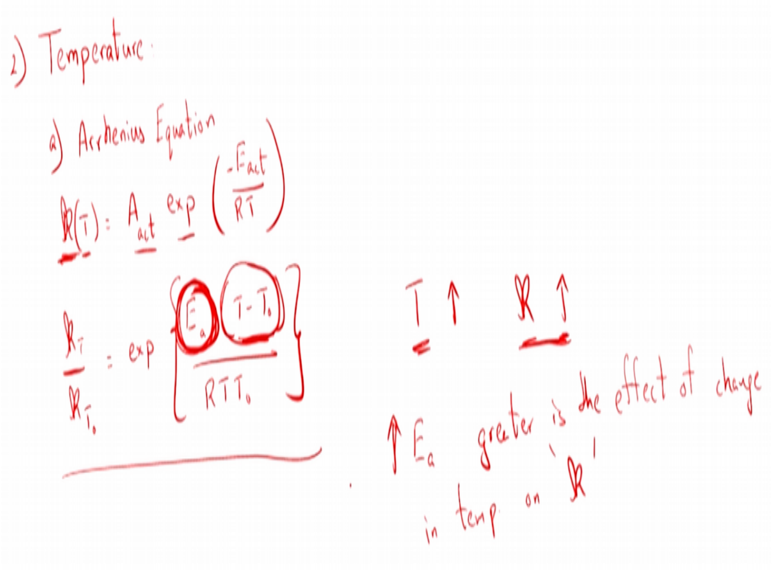

So temperature in general this is the rate constant now at particular temperature activation constant is exponential of energy of activation by RT negative exponential I guess so rather than boring you with the not the calculating just athematic I guess right basic arithmetic basic calculation K at time T / KT = exponential of energy activation o T – T naught by RT naught.

So what is this mean as we increase the temperature right in general the kinetics of your particular reaction are going to be higher and that is something straight forward to do in general the rate constant not in general the rate constant going to be higher right the increase in temperature the faster the reaction it is and the second phase that needs to be looked at is that energy of activation of huge effect of your change in temperature on KT and we see why I guess and why that clear I guess.

So you need a small change in or change in energy of activation let us say will have a multiplying effect on your change in temperature here so the higher the energy of activation in general greater is the effect of change in temperature on the relevant rate constant so that is what you see here in this particular equation right.

So I think in different cases people might also have come across what is it now different empirical equations I guess right theta into T power – 20 and so on overall empirical equations that depends on the scenario that you are looking at right.

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c) Stoichiometry

$$\underline{\nu_A} A + \underline{\nu_B} B \; \overset{\cancel{\rightleftharpoons}}{\longrightarrow} \; \underline{\nu_C} C + \underline{\nu_D} D$$

-

- $\underline{r_{rxn} = k [A]^{\nu_A} [B]^{\nu_B}} \leftarrow$

$$\boxed{r_{rxn} = -\frac{r_A}{\nu_A} = -\frac{r_B}{\nu_B} = +\frac{r_C}{\nu_C} = +\frac{r_D}{\nu_D} \quad ?}$$

$$r_A = -\nu_A r_{rxn}$$

$$r_D = +\nu_D r_{rxn}$$

So let us look at the other aspect here so stoichiometric I guess so why are you concern with stoichiometric here? So let us consider example here example reacting I guess stoichiometric coefficient of A in compound A, B that can go on to form or let us say I am only going to reaction here form C this is not R this is stoichiometric coefficient I guess right D right.

So here what is the rare of this reaction what is the rate of this reaction take a few moments to think about that right the rate of the reaction is going to be what now the rate constant of this particular what do we say equation right multiplied the concentration of A raise to the power of stoichiometric coefficient into the other reactant B raise to the relevant stoichiometric coefficient this is the rate of the reaction though right.

But in general we do not just want to have an information about rate of the reaction though I want to know how it relates to rate of change of A rate of change of B rate of change of C and rate of change of D right I want to be able to come up with the metric that can equate all these aspects and how do I do that I guess and obviously relate that to rate of the reaction here and this is the rate of the reaction right.

So for that particular case I am going to look at the stoichiometric coefficients and I think we looked up these but trying to define the calculate delta G and so I am going to normalize this by the stoichiometric coefficients right and another aspect here A and B are being lost and C and D are being form so that is what you see here right. So this is a take home message is that you need to keep in mind right so what is this mean this more or less means rate of A = - because it is being lost stoichiometric coefficient of A into rate of your reaction right.

And for example D would be + because it being formed stoichiometric coefficient is D into rate of the reaction what is the rate of the reaction that is something we have here I guess right and so this is your basic stoichiometric so I believe we are at the end of our class but I need to still talk about one another aspect.

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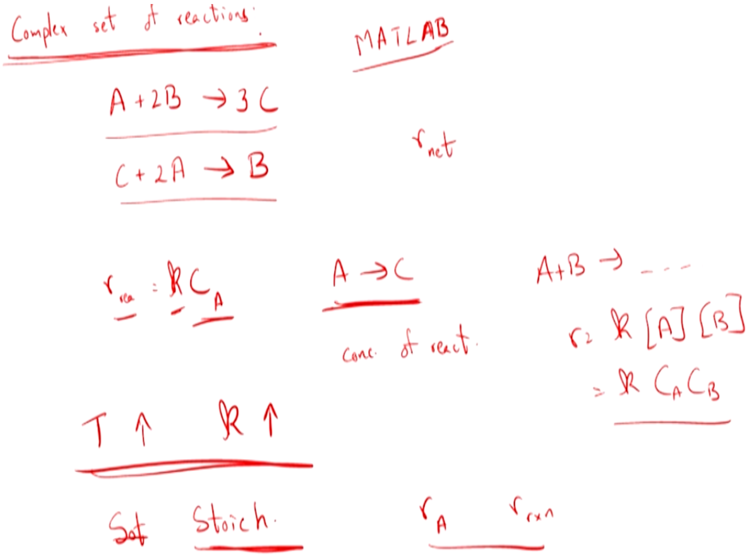

So the last aspect would be complex set of reactions now right how are you going to model the right and in general as you move higher chain right we are going to use matlab to model various what do we say phenomena we observe right and in general you cannot what do we say look at individual reaction and such their so for example we are going to look at A + 2 B going to C okay or 3C let us say and C + 2A going to D let us say right and so have let us say numerous touch cases right how am I going to go about it.

So I guess we will continue this in the next class or look at how to model or you know setup the relevant reactions we are going to look R net and such. So we will briefly discuss what we looked up today and then wrap it up I guess right so we still taking about kinetics and how rate of the reactions is depend upon the concentration right and it is typically KC for A going to B concentration of this is what we looked at right.

And we only always look at concentration of your reactants right we always look at the concentration of reactants the rate of relevant reaction here which is A goes to C which is fully depends upon concentration of A and obviously the rate constants here right and if it is A + B going to whatever it is here relevant rate is R = K into concentration of A into concentration of B right that is what we have here second order here right.

And we also looked at the effect of temperature in general the greater the higher the temperature the higher the rate constant or higher the kinetics are going to be right and then you also looked at effects of stoichiometric right and how to relate the different rates of your particular compounds with respect to the rate of react in general we are going to look at complex set of reactions in the next class and I guess that is it from me now and thank you.