Environment Engineering: Chemical Processes
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Module No # 02
Lecture No # 07
Reaction Kinetics

Hello again we meet again I guess so we were discussing concepts related to equilibrium in our last class right. So first we will talk about or review those aspects and then take a holistic view of what we have discussed so far because now we are going to move on to another major topic or one of the other fundamental that we are going to discuss about and which is the kinetics right. So first look at what we have discussed in yesterday's class for now I guess here.

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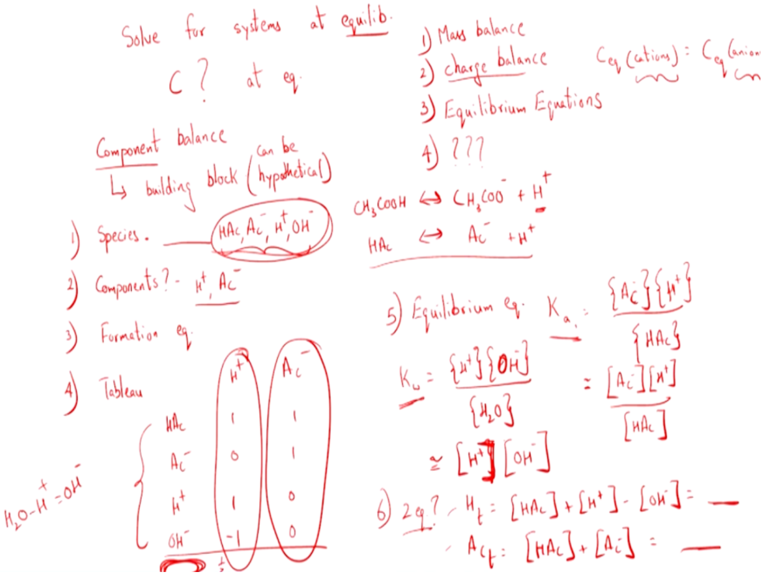

So I believe we were trying to solve right systems at equilibrium right I mean I want to know what are the concentrations of various compounds at equilibrium and what are the equation that I can use I can use mass balance if applicable or depending upon the scenario I can also use charged balance right. More or less what this is mean the concentration equivalent of all the (()) (01:37) will be equal to the concentration equivalence of all the anions right.

But rarely will we have complete how you know comprehensive all the knowledge about all the cations and the anions so this has limited applications I guess. But in general charge balance is always fallen right. And then we obviously looked at equilibrium equations but as we noticed in last few classes or couple of classes in any way we have still missing a few equations to be able to solve for our unknown.

So what is this set of equations I guess so in this particular context we introduced component balance right so what is that mean I guess we are going to introduce a concept of building blocks so this can be hypothetical can be need not be though right and what do we end up doing I guess we will review the process so we look at or list the species and what are species these are the actual compounds that exist in the solution at equilibrium right.

And depending upon the species so let us take an example I guess you let us take CS3 COOH dissociating into its conjugate base right and dissociates by the giving out its proton right so I will approximates this by saying HAC acetic acid state ion and H+ right. So what are the species here we know that we will have HAC and AC – and we will also have a H+ whenever we have a H+ we will also have a OH – obviously water is always species but we are not going to list that I guess right and what next.

So we need to choose components and how do we choose this components we choose them such that you know the minimum possible number or combination would be able to give us all the relevant species so thumb rules we always choose H+ or we try to rather and choose the most deeper pertained form of the particular acid and which in this case is the A state ion right and then I believe we said formation equations so I am going to skip that for now right.

How are you going to form that relevant species from the various components and then from the formation equations it will be able to find the tableau and what is this tableau about it is have the idea about the component balance so here we are going to do that I guess H+ and AC – the component they are and all the species here H+ AC. AC- H + and OH – right how many H+ do I need to form AC1 0, 1 and – 1 and Y is OH – negative H+ because it is H2O – H + = OH – right.

So again AC – 1, 1, 0 and 0 and if I know based on what it is what is the initial solutions that leading to or source of all these components we can that equate that here so next stop I need to write my equilibrium equations equilibrium equations right and in this case we have two equilibrium equations one is the acid dissociation and constant here K1 = activity of AC – or state ion into activity of H+ right by activity of HAC.

So this is the acid dissociation constant anyway we are going to discuss this in greater detail later on you know for now please bear with so obviously we can in dilute solutions we can approximate by this concentrations or relevant concentrations right so activities we are now approximating them by the concentrations right and other one would be the water dissociation H+ and OH – by activity of H2O and obviously activity of H2O is going to 1 and gong to approximate them by concentrations right.

But still we have only two equations here right K1 K to the equilibrium equations and we have 4 unknowns here seems species right so what do we need to do we need to come up with to addition equations to addition equations what are those do right and that you will use to component balance.

So if you look at this I am going to balance the components and whatever the transformation within the systems or between the species the total components are going to stay the same that is the concept here with respect to component. So H total = what now concentration of HAC + concentration of H+ - concentration of OH – right and what about ACT total? Total ACT is either going to be HAC or AC – and if you know what the source of these compounds is have with you and we have now two additional equations.

So we have 4 equations and 4 unknown we can solve for that accordingly right so with this particular aspect of component balance we can now calculate you know what are the equilibrium concentrations of any compound actually give an the relevant condition this always works so out their either from different instructors or from let us say now a gets internet is I guess popular with the people right but anyway their might be multiple ways out there to solve various problems.

But one aspect or one way any way that would never fail is the component balance equation a generic approach which always works right and here we are going to use through the class that is the fundamental here building block here for our class I guess right. So we are done with equilibrium for now so we are going to move on to the next immediate topic which is kinetics but we are very briefly going to talk about or look at what have discussed so far in the class right.

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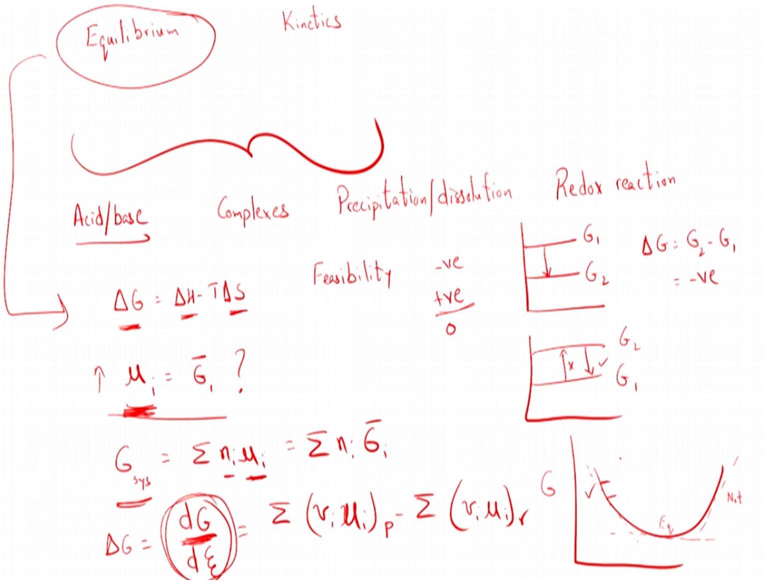

So I am going to look at now equilibrium now right so again we divide our class into equilibrium and kinetics right and then we are at the later stage of our class going to look at the applications of these two aspects you know with respect to most commonly used for you know reactions or most commonly what we say the reaction that we come across as an environment engineers in general acid base and then complex formation or say complexes let us say complexes precipitation and dissolution and more importantly redox reaction the oxidation and reduction reaction right.

So this is what we have for the later part of the class so thus far we have talking about in the fundamental here related to the equilibrium right. So what have you discussed thus for let us say I believe we mention that it is driven by thermodynamics right and thermodynamics we need to look at delta G values that is equal to delta G delta S and then we looked at feasibility of particular or particular reaction right.

When at negative we see that it is feasible when it is positive not feasible at reverse reaction is feasible I mean 0 it is at equilibrium. So obviously for visualization purpose we looked at you know state G1 and state G2 so higher energy state right so it can fall down the ladder to G2 and delta G here is G2 – G1 and you can see here that G2 and that can go through though if it is inverse though obviously it is going to be not feasible there for example of its G2 and G1.

G1 cannot move up the ladder to G1 so this would not happen but G2 can fall down the ladder into G1 right again that is what we say and delta G is positive anyway and then we looked at have enthalpy of its delta G how entropy of degree disorder effects the Gibbs change in Gibbs energy and so on right and then we believe we looked at concept of chemical potential for a particular compound and that is equal to the molar Gibbs energy of the compound.

So chemical potential what is that i guess for gives us and idea right about potential for a compound react chemical potential you know the same potential of a particular person or particular company or such here I guess here right I am just drawing natural simpler receiver right chemical potential here. So greater the potential greater the chemical potential greater the potential for the compound to reach and then fall down to a lower chemical potential here that something we came across their and then we believe we applied the what do we say G systems or came across calculating the Gibbs energy of system.

And I believe what did we have NI Mu I NI is the moles of particular compound or component Mu I is the chemical potential of the that particular component also that similar obviously to Ni NG bar summation of Ni NG bar or product I guess and so then we looked at applying that too reaction and I believe looked what is change going to be and so on and I believe we came across for generic reaction VI Mu I of the products – of the reactants this is what we came across obviously what is particular set of variables I guess are the variable here the differential here.

So how does the Gibbs energy of the system change with small change in the reaction or when the reaction as gone through the small extent let us say. So that is nothing but obviously delta G right so obviously when we do the particular figure here and we looked at one particular schematic G of the system. So when the slope or this particular variable DG by DZ is negative we see that the reaction is feasible and then it can fall down from a higher energy state to a lower energy state right.

So anyway the slope is going to be negative here and when it is equal to 0 when the slope is equal to 0 and we see that it is equilibrium and again it is positive we see that it cannot move up to ladder not feasible here not feasible here and I believe we this is what we looked at and what else the we look at I guess.

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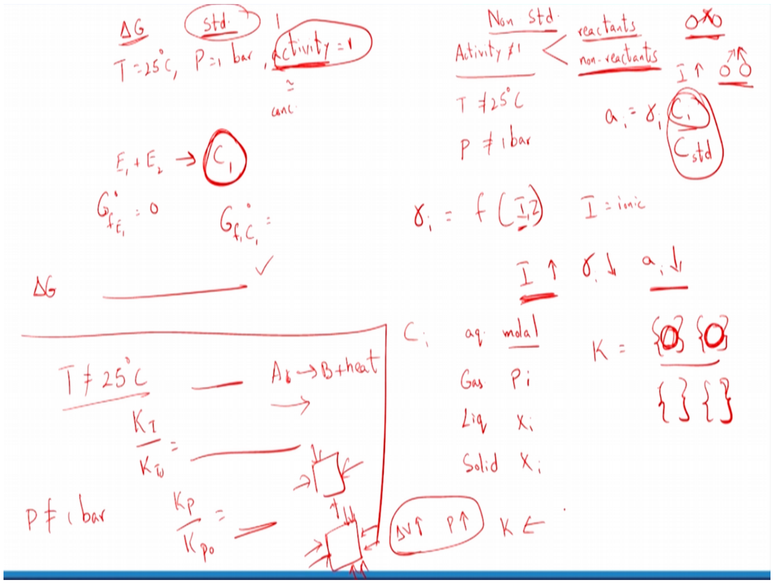

Then we start looking at how to calculate delta G values at I believe standard condition and then non-standard condition right. So standard condition we define them as temperature = 25 degree centigrade and what else = 1 bar and came across the new what we say the term called activity of the compound or component and we said activity = 1 it is a standard condition right.

Activity I guess is that time approximating at concentration right and gives us an idea about the ability of the particular compound to react right and so we came across this I think we mention that we can look at the elements you know leading to the formation of particular compound right and then we define the Gibbs energy of formation of these elements as = 0 this is our reference so from that we can come up with measure the Gibbs energy of formation of the compounds at standard state we can measure this right.

And with these you can come up with any other reaction or delta G values for a any other reaction that you want to and this what we looked at in this particular standard conditions right and then we looked at standard conditions as in what would happen to that system or how would the system change with respect to the delta G calculations and such if the activity is not equal to 1 which is what would have observe if it is not equal to 1 or if the temperature is not equal to 25 degree centigrade and pressure is not equal to 1 bar right this is what we looked at.

So with respect activity not equal to one there are two aspects one is the reactants themselves and the other is the non-reactants. So in general we mention that two molecule they collide you know right and then the reaction takes place so the higher the number of what we say the reactants or the concentration of the reactants the greater the possibility for collation and thus the greater the feasibility of reaction.

Again when we have charge species this is what you would see or a respect in your solution or you have a multiple non reactants that are charges and if the ionic strength is high that we can have a detrimental effect of the interaction between the two relevant compounds or three or four right. So that is why we looked at activity I guess right and what did we define activity as activity of a particular component or compound = activity coefficient time is normalized what do we say what i this now the dimensionless concentration of that particular compound I guess right.

So for that particular aspect we will had different particular equation for activity coefficient almost all of them are function of I and what is I is the ionic strength right and higher the ionic strength the lower the gamma I and thus the lower the activity of the particular compound that is obvious I guess the higher the concentration of non-reactants that you are going to interfere with your reactants let us say the lower is going to be ability to react let us say.

So that I what we have here that was the take home message here right and obviously here I define what are units we need to look at with respect to the concentration of I here and believe for the aqueous phase we said we need to use molal not molar here and if you use molal then we error of what I think 3% here in this case. So aqueous phase and then gaseous phase it said it is going to be what now partial pressure and in the liquid phase and in the solid phase it is going to be the mole fractions of the particular component so that is how we define that right.

So what is that mean as if I have equilibrium coefficient = activity of this thing and so on right and need to write down the concentration here what am I going to do if I am aqueous phase here I am going to use molar concentration if I have the gaseous component here I am going to use a partial pressure here right so that is what more or less translates into and then we started looking at what are the effects of temperature non being = 25 degree centigrade right.

I think we looked at (()) (17:06) equation and I think we looked at relevant aspects in general right but I specially with respect to general reaction this is what we looked at I guess example we are not going to go in detail now in general the greater the what we say temperature greater the kinetic energy of the molecules and greater the chances for collusion and chances for reaction going through and that is in the general case but we looked at relevant equation for KT / KT naught for relevant scenarios and we looked at them right.

And then we also looked at what would be the case when pressure is not equal to 1 bar or the standard conditions and then we looked at the relevant aspect again K at P pressure at K at the P naught standard and how that various and in general we know that let us say this is the current pressure of 1 bar and let us say now we are applying twice the pressure let us say right so this is going to resist of the higher pressure the greater the resistance to change in volume right.

So whenever the delta V needs to increase say if you are increasing the pressure that will be to the betterment of the reaction because you obviously need not betterment I guess the equilibrium coefficient is going to shift towards the left yes and the this what we discussed in the class say again we are not again going to go into that in greater detail right.

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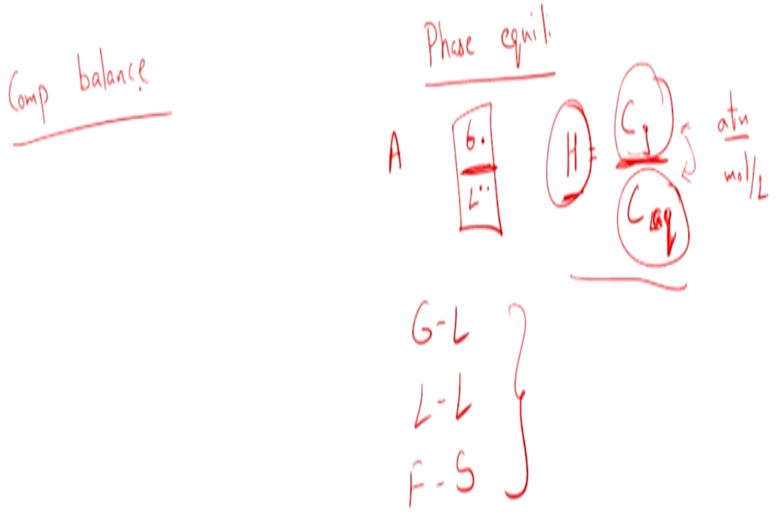

So I believe the last aspect then we end up covering I believe this looking at the component balance I believe right and before that we also looked at phase equilibrium right. So particular compound let us say compound A if it is in particular phase 1 as in gaseous or liquid gas right it will equilibrium between these two phases now.

So one mole in gas two moles in liquid and so on and so we came up with relevant relationship and think one for this particular case is the henry's constant right that gives us relationship between concentration in gaseous phase and concentration in the liquid phase I will in general the aqueous phase here I guess right.

And keep in mind that the units of henry constant can be different so actually someone defines the units in different way you can even have the inverse of this particular fraction here right you just need to look at the units before you come up with your particular term or look at your particular units of your particular individual variables here right. So it can be atmosphere per mole or moles per what we say liter right this is one particular combination of units per henry's constant and there can be particular other equations.

And so same case we looked at gas liquid, liquid – liquid and fluid and solid what do we say phase equilibrium and we looked at how it goes about and such right and we looked at generic example and then we came across component balance with which we discussed today right.

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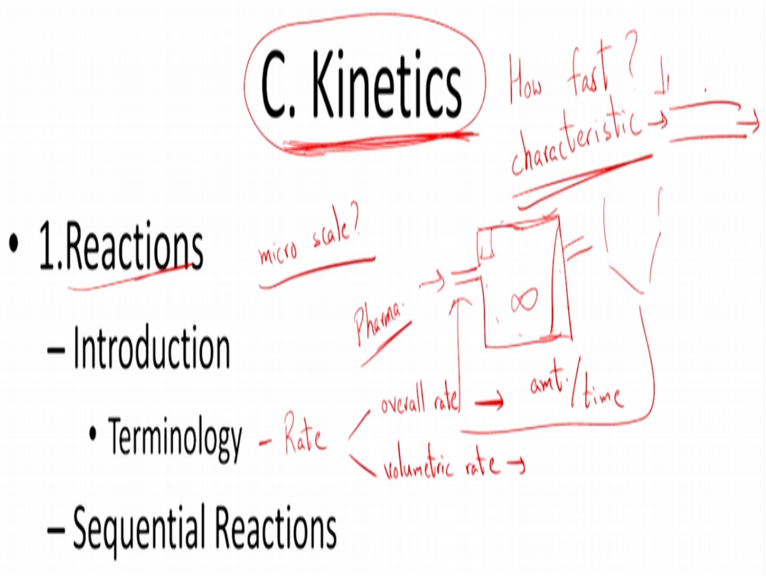

C. Kinetics

- 1.Reactions
  - Introduction
    - Terminology
  - Sequential Reactions

So anyway now we are going to move on the next major topic which is the kinetics right and kinetics what gives an idea about I guess gives us idea about how fast is the process chemical process right how fast is it? And as we talked about it is a characteristic it is not a state obviously it is a characteristic of particular process. So right we usually apply them to reactions at micro scale and why do you need information about kinetics let us say right.

For example let us say you have an activity sludge process here I am in a poor what do we say yeah very poor with respect to drawing figures here so should excuse me I guess right. So let us say you can activated sludge process here right and with the return here and so on and this is where your reactions occurring here let us say you want to you conducted the test in your lab let us say right and you want to obviously scale this up.

So what do you need to look at though you need to look at the relevant kinetics right the kinetics of particular compound let us say now most people are looking at emerging contaminant or let us say talk about a pharmaceutical compound let us say right a pharmaceutical compound entering here and you want to see what how fast or if any is your particular compound being degrade in your activity sludge process right.

So you will connect the relevant lab test after regression you will come up with kinetics and then you can use that to scale up your particular model later on right and apply that your engineering systems to yes. So with respect to terminology we usually come across rate of reaction right and in general we will use two aspects mostly one we will discuss two here overall rate and volume metric rate right and overall rate as it indicates guess is just amount of substance degraded of form per time or change in amount of that particular compound per time.

But here you know let us if you apply this ASP let us say we are not talking about with respect to volume though right. But that going to create issues if not in ASP if you have a river let us say right you are dumping a compound here river is flowing in this direction right let me draw better figure here right.

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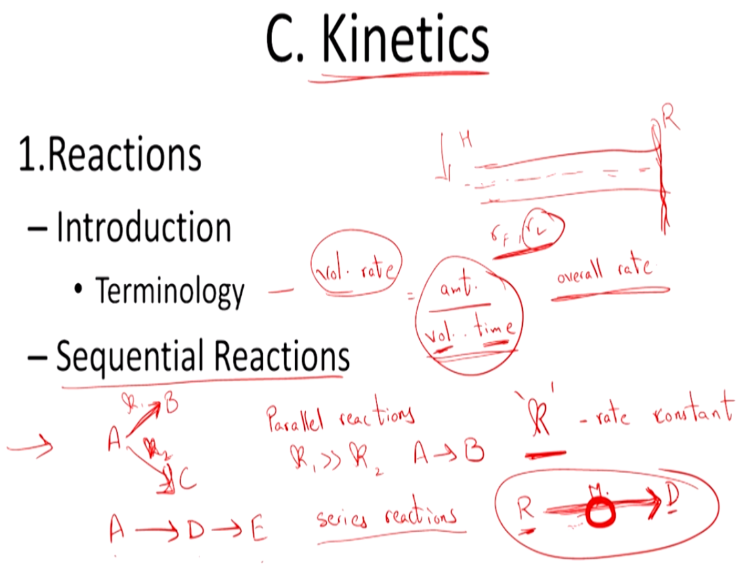

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So we have a river flowing through right let us say this is Haridwar somebody is dumping industrial waste and I am at Roorkee here and I want to see this particular compound here by when it reaches me at roorkee right so for here though as we see the reaction are occurring throughout the course of the river I will have obviously the transport mechanisms advection what do we say diffusion but obviously you are going to have either rate of formation or loss of your compound and I want to be a able to look at that.

So if I look at the overall rate that will give me the misleading picture or incomplete picture right so what do I usually for I go for a volumetric rate and that is nothing but change in amount of your substance per volume per time right so that is what you see here right. In general this is what we are going to use volumetric rate throughout the course of our class yes and that is amount of our substance that is transformed per volume of our particular system per time let us say right.

And in general the next aspect is going to be the sequential reactions so let us say if I have a compound A in solutions right it can transform into multiple ways right in the real world it can either go or degrade through parallel reactions B and C right here A into B and A going to C are parallel reaction right. So here you can have parallel reactions the same time you have a piece of series reaction pardon me series reactions right.

So we are going to discuss these two aspects in greater detail and why so for example let us say if I now looking at the particular case with respect to A degrading where two reactions and those two are parallel reactions A going B and A going to C are parallel reactions. So let us say if you want to mode of this right and you are going to look at let us say for example you know that A going to be is remarkably faster than A going to C.

You know let us say 1000 times than magnitude let us say at the rate constant we are talk about what great constant is later on for now think of it as metric that give us an idea about how fast the reaction is or about the kinetics of the reaction so again we are talking about the new term rate constant and this is a small K I guess right rate constant. So let us say rate constant of going to B K1 is far greater than A going to C right.

So I can then neglect A going to C and just say it is just A going to B right simply my set of process and then the next aspect is going to be the series reaction right when A goes to D goes to E right and in this case what I am concerned with let us example think of this say as I go from let us say Roorkee to Delhi let us say and assuming that you know this is hypothetical case I guess right that free of traffic.

What do we say what do we say highways here right what do I need to look at? I need to look at where I have major population let us say I think I come across Modi Nagar and Ghaziabad at this particular point in space right I am going to be stuck in traffic right half an hour or 1 hour right. So if I looking at rate of my traffic travel from Roorkee to Delhi what defines my in general travel now right at that particular point in time or the rate into step right.

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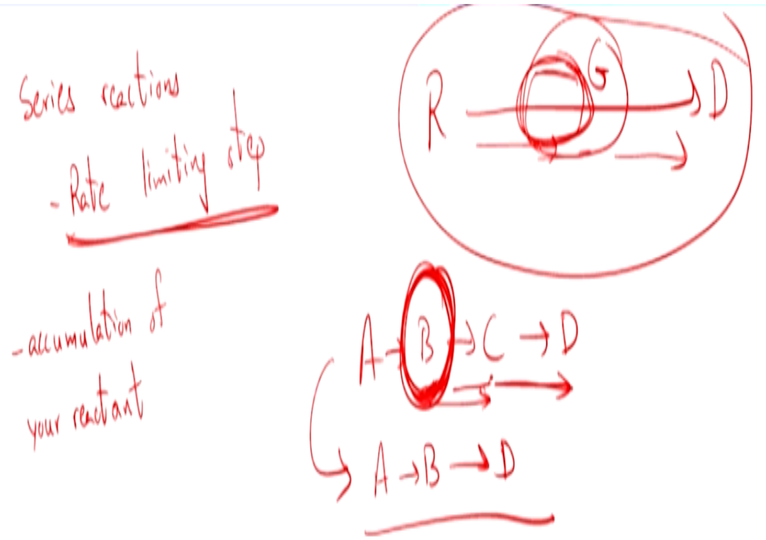

So this the new term that we have in your series reactions you have a rate limiting step and the (()) (26:42) we are looking at is travel from Roorkee to Delhi I hate traffic in Ghaziabad or Modi Nagar and here the traffic piles up here for many what do we say kilometers or so right. So here irrespective of rate which I come here or here crucial aspect I am concern with is the rate at with particular point in space.

So similarly in reaction let us say I can have A going to B going to C going to D and so on but it let us say B going to C or slow you are going to have a lot of accumulation off compound B right so you can say that A going to B goes to C D I guess that because B to C and then pardon me D to C is the fast reaction let us say. So I can approximate this particular series reaction by saying A goes to B goes to D.

So in general rate instinct step is when you have accumulation of that particular compound or the reactants you will observe accumulation of your reactants right that is the rate limiting step here and in this case the reactants is going to be B as that accumulating because B going C is very slow right that is what of your reactants think of that as accumulating at particular traffic jam or junction here in your travel case I guess right.

So I believe I have a set of what do we say graph to look at but I believe we are running out of time so we will discuss this in next class and for today's session that's it from me I guess.