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Lecture No. # 06 Chemical Reaction Kinetics and Reactor Design

Friends, let us continue our discussion on chemical kinetics, and last time we saw several restrictions that come on the rate of reaction, because of thermodynamic consideration. To recap what we saw last time we said that if the reaction is reversible, then the rate of forward rate ratio of forward rate constant to backward rate constant is the equilibrium constant. Because of this we do not have freedom of choosing both forward rate constant and backward rate constant independently. Because thermodynamics specifies for us what should be the equilibrium constant. So, if we choose any one of those constants, the other one is automatically fixed. The same applies to power law kinetics, and the orders that we use with respect to forward reaction and reverse reaction. Let us continue this discussion further and see what happens when we have a reversible reaction taking place in the reactor, and to get a feel of how reaction rate changes as these reaction progresses, let us look at in qualitative terms.

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So as we saw last time we start with reaction summation nu j A j equal to 0 taking place in the closed, isothermal, constant pressure system. And let us say that this reaction is reversible reaction. So what we have is forward rate backward rate, so forward rate k f into product of C j raise to q j product overall species. Similarly, backward rate k b into C j raise to q j prime, and we also said last time that for law of mass action kinetics q j and q j prime are link to the stoichiometric coefficient nu j by these relations; that is q j is half of mod nu j minus nu j, and q j prime is half of mod nu j plus nu j.

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Now let us see how reaction rate varies as the reaction progresses. So, we have these rates of reaction which is forward rate minus backward rate, which is power law kinetics as expressed over here. Let us bring our definition of extent of reaction so C j is C j zero nu j into alpha. Now you we have seen in the last class that these rate constants depend on the temperature that is this rate constants k f and k b are functions of temperature. We see that concentration is a function of extent of reaction. So concentration is a function of extent of reaction. Now we have rate of reaction explicit function of extent of reaction and temperature both forward reaction as well as reverse reaction.

Now, what happens when the reaction takes place in a closed isothermal system or closed system? We have alpha that is zero at the start of the reaction and it progressively increases. Now in a non-isothermal system temperature also can change. For a isothermal system temperature is constant but for non-isothermal system temperature also can change. So the question now we ask ourselves is what happens as reaction progresses? We are not worried about what reactor and so on. We will worry about it in the latter half of this session.

But just say that alpha changes and temperature also may change. So depending on how alpha and temperature changes the rate of reaction been changed. Now how alpha and temperature changes will depend on what reactor we are using how we are operating and so on. At this moment we are just considering for sake of illustration that alpha and temperature is vary, so for different values of alpha different values of temperature how does the rate of reaction change.

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So to see that we see some rate contours here, but before we come to this little bit of background; so let us go back to our reaction and we have our reaction summation nu j A j equal to zero that is our reaction and exercise just now showed us; that we can express r as r f of alpha and T minus r b of alpha and T. So we have forward rate of reaction backward reaction rate. Now what we want to see is how these rate changes as alpha and T changes. Now alpha and T are two variable so if you were to plot rate as a function of alpha and T one would require a three-dimensional representation alpha on one axis, temperature on one axis and rate on another axis.

Let us see that is little complicated. So instead what we will do is we will try to see how the rate of reaction varies in a slightly different form. We will try to see the rate of these reaction contours that is how assuming that r is some constant value C. How does that contour look like in a phase plane of alpha and T? So what we are going to see is a twodimensional representationon one axis y axis we have alpha or extent of reaction on x axis we have temperature and so given a point; we will try to see how does the rate of constant the contours of constant rate look like in this phase plane.

So what does it mean it means that if i take all those values of alpha and T for which the rate has a constant value C; this becomes my contour and join all those points these becomes my contour for rate being constant. So any combination of alpha and T on this contour all gives rise to the same rate C. So that is a that is how we view this threedimensional picture into a convert this three-dimensional into a two-dimensional contour contour plot and we are going to see this for variety two different cases; when reaction is endothermic and when reaction is exothermic.

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Now the background for this is as follows; so we have what we are saying is you are going to see this contours for constant rate and in order to see how these contours vary let us also do one small exercise and take partial of rate with respect to temperature and if you do this differentiation by plugging in power law kinetics into this two rate into this two rate forms; we will end-up with this particular form. I leave this to you I leave this as a small exercise for you to do but we get this particular form. What is E and E prime? E is a our we have a kinetic rate constant k f and which is A f e raise to minus E f or let us put or E by R T r to make matters clear let us put f and b over here. So E f and E b are the activation energies for forward and reverse reactions respectively.

Now it tells out that going back to our thermodynamics; we can also show that E f minus E b must be the heat of reaction delta H or enthalpies P change. Now this is additional constant pose by thermodynamics where is you have heat of reaction you have activation energy forward and reverse reaction or backward reaction rate reactions and their difference must be delta H. So now let us go and have a look at how this contours look like first starting with when delta H is greater than zero or in other words we are looking at endothermic reaction we are looking at endothermic reaction.

> Rate contours - endothermic reaction Temperature

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First, let us look at how these rate contours look like and then we will come back to see, what these why these rate contours look something like this; what we see here on the y axis is the extent of reaction alpha and temperature. We jumped up one and went to exothermic reaction and but let us first complete with endothermic reaction and then go to exothermic reaction. So first let us try to see what does these contours are showing us. So what these different color things that you are seeing is actually the contours for constant rate; recall that we are looking at r equal to constant and what are those values of constant is shown in this color slide, which is on the right hand side.

So brown for example, denotes very high rate of reactions and as I keep saying time and again the numbers do not matter at this moment but qualitative information is what we are interested. So the rate that is this constant C is decreasing as we are moving down this color slide from brown to to dark blue. Now let us try to see what this contours are? The first contour that we can construct is the simplest one, which says that r is zero. What is r is zero? r is zero when the reaction has reached equilibrium and that contour is shown in this violet color line; that is the top-most line over here and which is a contour for r equal to zero that is our equilibrium line.

Now what does it say for endothermic reaction; we have already seen this in our earlier class that as temperature increases the equilibrium extent of reaction increases and this is that particular plot. Now for any other value of C we see that as extent of reaction increases or at a constant rather at a constant extent of reaction. As we increase the temperature the reaction rate is increasing that is if you let us say we just draw horizontal line at alpha equal to 0.2 then as our temperature is increasing this is a point where reaction rate is zero. So that is an equilibrium condition.

But as our temperature is increasing along this line we see that we are travelling from the color region which is the dark blue to brown through various different transitions; that means the reaction rate is increasing. Now why is this reaction rate increasing that is recall that we what we are seeing here is at a constant value of alpha; as we are increasing the temperature the reaction rate goes on increasing now to see why this is happening. Let us go back to our previous exercise that we did and we said that for exothermic for endothermic reaction E f minus E b which must be the heat of reaction is positivethat means why E f is greater than E b.

So now let us consider a scenario where we started the reaction with alpha equal to zero or with a low value of alpha. Now initially you expect that R f forward reaction rate will be higher than reverse reaction rate and E f is also higher than E b because reaction is endothermic. What it means is it are del T this is understood that this is at a constant value of alpha is always positive. Because del r del T is a difference of two terms, the first term is always higher than the second term; why because E f is higher than E b prime and r f is higher than r b and as a result we have this particular result that del r del T is always greater than zero.

In other words for a given value of for a given value of alpha for endothermic reaction del r del T is greater than zero and what does that mean in terms of this contours for a given value of alpha as we are increasing temperature as delta T is positive del r is also positive that is why the reaction rate will continuously increase and this is what happens when you have endothermic reaction. That is recall all along we are saying that alpha and T for sake of this illustration; we are changing them independent of each other. However that is not always the case because in a vector there will be certain relationship between how extent of reaction changes as or its variation is linked to the variation of temperature. So we have to worry about that link but will come to that in a minute.

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Let us go to the exothermic reaction and for exothermic reaction we see a different scenario what different scenario are we referring to if you look at this contours for example, this contour is always monotonic all these contours are monotonic. Now let us go to the exothermic reaction once again we see that we are saying r equal to constant contours starting with r equal to zero, which is this violet line and recall for exothermic reaction the equilibrium extent reaction decreases as temperature increases and naturally this is that contour. Once again our colour scheme is same we have dark brown, which represents high reaction rates to dark blue which represent lower reaction rate.

Let us go back and write this particular relationship which we saw earlier. Now let us see what what happens when you have exothermic reaction. So let me let me once again take the same approach of horizontal travel on given value of alpha. Now what do we see here. Notice the color change and that will tell you what what is happening to the rate of reaction. What is what is happening here? Low reaction rates are increasing as we are travelling the as we are traveling along this the color is changing from dark blue to light blue; that means the reaction rates are increasing increasing increasing, then beyond certain point the reaction rate.

Now notice the change in color from light green to the dark light light blue to the dark blue. That is the reaction rates are once again decreasing once again decreasing in this range. So what happened there in this range as we increase the temperatures the reaction rates increased but it started decreasing once again that is why there must be a point where the reaction rate is maximum. Now let me illustrate it at yet another level let say that we are looking at this particular value of alpha. And here you can now I once again clearly see that as the temperature is increasing the reaction rates are increasing increasing increasing. But then after some point the reaction rates are decreasing and eventually the reaction rates are going to zero.

Now why is this happening for exothermic reaction? Mathematically we can see in this particular relationship. Now according to our discussion earlier E f minus E b is delta H the heat of reaction and this is negative that is why E f is less than E b. So in this particular relationship E f is less than E b but initially r f is higher than r p and so del r del T is positive as a result of this combination. So in this particular region del r del T is positive. But what will happen remember our reaction is a reversible reaction of this kind. So initially the rate of A 1 going to A 2 is high but as time progresses as that is as reaction progress A 1 is going to go down and therefore, the rate of forward reaction will go down and the rate of backward reaction will come up.

Now E f is less than E b irrespective of where we are but r f which was initially higher than r b is now decreasing as the reaction is reaction is progressing. As a result there is a there is a region where r f E f will be much less than r b E b or in other words del r del T will be negative. Now the transition from del r del T positive to del r del T negative cannot happen abruptly. So there is a point such as this point this particular point where del r del T is zero. And what we see this white line over here is a tressing of all such points by repeating the same exercise that is you take this particular temperature rate increases increases increases which is maximum starts decreasing. So del r del T equal to zero.

So this is why now if we look at these contours what we see this contours are no longer monotonic; as they were before that is r equal to C is obtained by non-monotonic the contour is non-monotonic now its increases then decreases. Similarly, at all different different contours, so what we have here is very interesting behavior; that the rate increases initially reaches a maximum value. But then it starts it starts decreasing. Now qualitatively why is this happening once again mathematically; we saw why it is happening qualitatively it is $\frac{d}{dt}$ is for the following following reason. So if you look at this reaction A 1 going to A 2 reversible reaction.

Initially there is lot of A 1 so the forward reaction is happening at a faster rate compared to backward reaction rate and as we increase the temperature the rate constants are increasing so for a while the forward rate reaction increases significantly in comparison to reverse and we have increase in rate of reaction. However there comes a point remember this is a exothermic reaction with determines that as temperature is increased the rate of the equilibrium extent of reaction decreases; as a result after certain increase in temperature the thermodynamic constrains come in to picture.

Because now the equilibrium extent of reaction is limited when temperatures are high and therefore, the rate starts decreasing and eventually reaching the zero value; that is this equilibrium equilibrium line. So this is the conflict between kinetics and thermodynamics which is represented in this contour plot, kinetics wise temperature increases tend to increase the rate of reaction. But thermodynamic point of view for an exothermic reaction increase in temperature tends to decrease the equilibrium constant. Therefore, decrease the equilibrium extent of reaction therefore decrease the rate of reaction and the net result is for a while temperature as a positive influence.

But beyond certain threshold temperature starts actually limiting the reaction and this is true for exothermic reaction whereas, for endothermic reactions there is no such conflict. Both kinetics and thermodynamics are favorably affected by increase in temperature and hence we see this monotonic contours or contours which are always increasing in volume. So with this I want you to keep this information in back of your mind. Because when it comes to design of reactors; we will once again visit this to see how our reactor design for exothermic reactions is influenced by this kind of behavior.

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So to summarize we saw how we define the rate of reaction. For a closed isothermal constant pressure system, we define the rate of reaction as the rate of change of extent of reaction normalized by the volume of the reacting mixture if it is a homogenous reaction. If it is a heterogeneous reaction, we have several choices such as for catalytic reactions we do it by normalizing with respect to the weight of the catalyst. Then we have power law kinetics q j s q j prime forward reaction backward reaction order of reaction overall order of reaction. The rate constant k the simplest manner in which its dependence on temperature is expressed is an erroneous rate expression k equal to A E raise to minus E by R T where E is the activation energy.

Law of mass action kinetics is a specific case of power law kinetics where the orders q s are related to stoichiometry through a appropriate relationship and finally, we saw how the rate of reaction changes as alpha and temperature changes that is the extent of reaction and temperature varies. Once again I emphasis that what we saw these variation was for if we assume alpha and temperature can vary independently. We now bring in the mole balances or design equations for reactors, which will lead us to how these alpha and temperature temperature varies and this will be the topic of discussion for remaining of this session; that is design equations for reactors and we will naturally start to begin with ideal reactors and then look at some of the deviations from this behavior at sometime in future.

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So let us now focus on how the rate of how do we design the reactors for by considering the mole balances. So we are still reviewing undergraduate material and I should caution you when I say review some of this material, you may not have seen in this particular form but surely you have seen it in some form or the other. So design equations for reactors. We are going to consider ideal reactors and consider the mass balances and we will follow of this discussion by comparing different kinds of ideal reactors to see how we choose a reactor for certain processes.

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So what we are going to do to begin with is write a simple mole balance for the reacting species and once again we are going to say that we have N species A 1 A 2 N such pieces A N in which these reaction nu \mathbf{j} A \mathbf{j} equal to zero is taking place. But these reactions now taking place not in a close system but in an open system. So we have this reactor, we do not know what this reactor is but there is some reactor in which this reaction is taking place and as I said this is open system; so there is a flow coming to the system and flow leaving the system. So there is an entry point and there is an exit point for material to flow in and out of the reactor.

Now before we go to our mass balances few comments about the notation that we are going to follow so that we are all clear about what are the different terms we are talking about. To begin with capital F is the molar flow rate moles per minute and we put subscript j to denote that we are writing molar flow rate of species j and additional subscript 0 for denoting the entry point of the reactor. So F j zero for example, is the molar flow rate of species j that is coming into the reactor F j is which is going out of the reactor.

Then small v is the volumetric flow rate what we talked about is the molar flow rate moles per minute now we are talking about volumes per minute. So let say d m cube per minute and again v zero that is incoming v that is outgoing that means at the entry point v zero, exit point v. We have something happening in the reactor what is that of course, the reaction so there is a rate at which this species j is undergoing a change and let us write its rate as G j and G denote that will call rate of generation molar generation generation rate and again it is in moles per moles per minute.

V capital V is the volume of this reactor capital V is the volume of these reactors in which these reaction is taking place. Again when I say volume it is a volume of the reacting mixture, which could be seventy percent eighty percent of the reactor volume but that is how we understand the concept of volume. C j is the concentrations moles per volume unit so it is nothing but the ratios of corresponding capital F and small f and t is the time let us say.

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Let us do a general mole balance and see how we get this particular mole balance. So let us do this balance for a small volume so that we follow the steps that are inward. So let me emphasis again this is my reactor the rate of generation is G j whatever is coming is F j zero whatever is going out is is F j and we are clear as of whatever different terms that we are going to use one more term that we are going to use is N j which is the moles so this is in moles mass. Now we do a simple regular mass balance mass in minus mass out plus generated must be what is accumulated in the reactor; that is our standard typical mass balance for any process chemical reactions is no exception, in out minus out plus generated equal to whatever is accumulated.

Let us say that we do this mass balance over a small time step delta t. So in time delta t how was the mass that has come inside the system if F j zero is the molar flow rate moles per minute then F j zero into delta t must be the mass of j that is coming in the reactor. What is the mass that is going out of the reactor? It is F i so during same time interval delta t F j must be the mass that has left the reactor or the system. How much was generated? G j times delta t. G j is the rate of generation in the reactor so in time delta t G j into delta t must be the moles. Note that all these individual units are in moles moles of species j and how much would have accumulated inside the reactor.

Accumulation inside the reactor is N j at time t plus delta t minus N j at time t. Here all we are saying is this were the moles at time t delta t and if this were the moles at time t then in time interval delta t this difference is how much has accumulated in the reactor. Now if we divide the whole the both sides by delta t and take limits as delta t goes to zero we get our mass balance equation F j minus F j zero minus F j plus G j is d dt of engine. Since we are dividing this mass balance by delta t, what we have is the now expression in terms of rate each of this unit has each of these term has a dimension of rate now.

The left hand side or let start with right hand side, right hand side is the rate of accumulation of species \mathbf{j} dN \mathbf{j} dt which is the result of what is coming in F \mathbf{j} zero minus F j what is going out and G j the generation rate into that must be the the net rate of accumulation. Now we know what inlet outlet is and so on. Let us spend some few minutes on what is this generation rate? Now generation rate we said that it is in moles per moles per minute. If we for example, assume that the working conditions are such that there is no variation inside the reactor variation of temperature or concentration or any quantity that influences the rate of reaction that is temperature is uniform all throughout, concentrations are uniform all throughout and you would have by now guessed; we are now talking of perfectly mixed reactor reactor in which there is very good stirring.

So that there is no variation within the reactors to put at formally there is no special variation of concentrations temperature or any other quantity that influences the rate of reaction if that is the case then our earlier definition of rate of reaction r j, what were its units were moles per d m cube per minute let us say. The rate of generation of species j recalls that r $\dot{\mathbf{i}}$ is nu $\dot{\mathbf{j}}$ into r, where r is the rate of reaction. I keep repeating this thing because I believe certain degree of repetition does not harm anybody. So we have r j as the rate at which the species j is undergoing reaction and its same throughout the entire volume if that is the case then r j multiplied by the volume of the reactor must be the rate of generation; the total rate of generation of species j that is G j. So if there are no special variations then we have this particular G j which is r j into V so that that is the balance.

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 $Q =$ moles - mass out $F_i \Delta t + G_i \Delta t$ $F_{j} + G_{j} =$ $G_j = \sum_{k} Y_j \Delta k_k$

So, now let us go back to our mole balance and let us go back to this particular expression before we actually move to looking at the set of equation. Now this is what we said is the case when there is no special variation but let us say that there is a special variation that is things are not uniform in these reactor. So what we can do is consider small volume elements delta v 1, delta v 2, delta v 3. So these are all small volume elements delta v, and in this volume element let us say v k r k is the rate of reaction $\frac{r}{r}$ k is the rate of reaction. So in this volume element k delta v k sorry delta r k rather r k into delta v k must be the rate of generation in this volume.

But there are so many other elements, so we can we can add-up all the contributions from all these small small volume elements. So let say that summation r k delta v k over the entire set of volume elements small volume elements this must be now my generation rate G j. So what we are saying is that we are now looking at this system consisting of small volumes delta v in which things are uniform, this is just for argument say and contribution to the net rate of generation of species j is coming from each of the small volumes and each of the small volume has a contribution r k into delta v k, where r k is the rate in that particular element and delta v k sorry r j.

Let me write this once again r j is the rate in that particular volume element times delta v k. So we can write this as $r \in \mathbb{R}$ is that is the rate of generation of species \mathbf{i} in the element k and volume of that element and summed over all this k. Now once again we can make

these volume elements smaller and smaller and smaller such that delta v k tends to zero, then summation of series is converted into integral and what we have is G j is integral r j dV that is summed over or integral over the entire volume v is my net rate of generation.

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So now let us go back and this is what is that mole balance that we get, that is F j zero minus F j plus integral r j dV is dN j dt. Once again molar flow rates molar flow rates the intrinsic rate of reaction or intrinsic rate of species variation r j per unit volume times dV summed over the entire volume is the rate of accumulation. Let us now simplify this mass balances for various difference scenarios.

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So going back our mass balance general mass balance equation is this. Let us consider a batch reactor. In a batch reactor we know that there is no in flow, there is no out flow that is why both these terms disappear and stirred time reactor operated in the batch mode. So conditions are uniform throughout the entire reactor and we have dN j dt as r j into V as our mole balance straight forward exercise.

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Let us see what happens for a continuous stirred tank reactor operating at steady state that means when steady state is reached. So once again we have we are doing the steady state balance and for a stirred tank reactors where here is a material coming in material going out, at these rates of F j zero and F j at steady state so this is zero. We are left with F j minus F j zero minus F j as minus integral r j dV but once again we have uniform conditions in the reactor. So this is nothing but r *i* into V and we have our mass balance equation for a stirred tank reactor V equal to F $\mathbf i$ zero minus F $\mathbf i$ by minus r $\mathbf i$.

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What happens for a plug flow reactor? There are various ways of looking at it, but let us go back to our generalized mass balance equation dN j dt as F j 0 minus F j plus integral r j dV. Recall for a plug flow reactor the fluid moves into the reactor like a plug. So, one part comes in then we have entry of next part it pushes the part further, and there is a continuous movement. There is no mixing or communication between the fluid elements, which are in the reactors. So it is a just like a plug.

So we can simplify this mass balance equation at steady state this is 0, and we have $F \in \{0\}$ minus F j, which is minus integral r j dV and we can differentiate this with respect to V, and express this thing as d dV of F j d dV of this whole quantity F j 0 is fixed. So d dV of F j is nothing but rather minus r j or dF j dV equal to r j. This is our mass balance equation for a plug flow reactor. We will stop here, and then continue this discussion by looking at how do we compare the performances stirred tank reactor, and plug flow reactor in our next session. Thank you.