Chemical Reaction Engineering

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Module No. #02

Lecture No. #05

Chemical Reaction Kinetics – Overview

Friends, let us continue our discussion on Chemical Kinetics. And in our last session, we defined the Rate of the Reaction. So, we have a reaction, summation nu j equal to nu j A j equal to 0 that is our standard reaction; and we defined the rate for a closed isothermal constant pressure system, as rate of change of extent of reaction, that is d alpha d t normalized by the volume of the reacting mixture.

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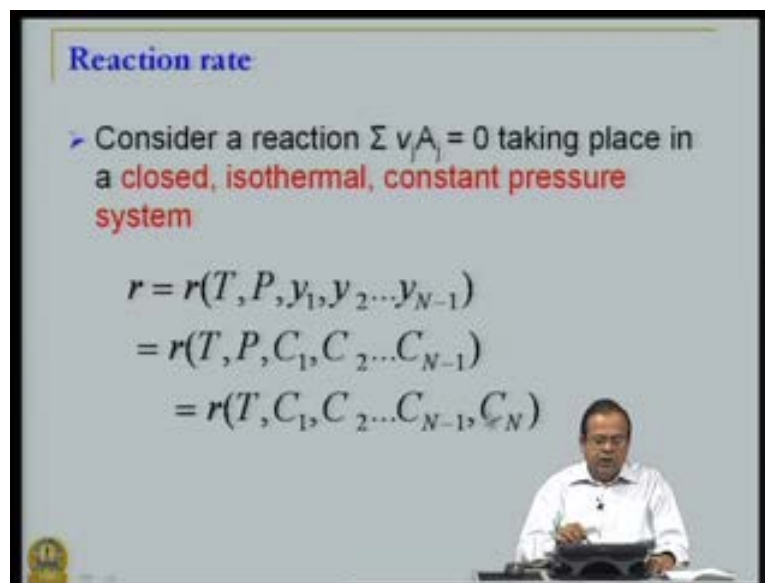
I mentioned in my last class, that if you are dealing with homogenous reactions, this V is the volume of the reacting mixture. But, if you are dealing with heterogeneous reactions, which involve more than one phase, the normalization could be by different several different ways; for example, if you are looking at gas-solid catalytic reaction, then the normalization could be by the volume of the catalyst or by mass of catalyst. So,

appropriately we will define rate as d alpha d t, 1 over w, for example is the weight of the catalyst that we are using.

We know our extent of reaction is defined as n j minus n j 0 by nu j and so, if you take a derivative of alpha, we can now define rate of change of species j as 1 over V d n j d t, and as we saw in the last class, that r and r j are related to each other or u j into r is simply r j. So, now, let us continue our discussion further and try to see, what kind of mathematical expressions we can expect for rate of reaction.

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So, let us let us consider the same reaction, and now, our objective is to find out, how rate depends upon the operating conditions. Recall that, in our discussion on thermodynamics, we talked about, how equilibrium constant, and therefore, extent of reaction depends on operating conditions. Now, our objective is, how this rate depends on operating conditions; and we could choose various different ways in which, we could express this dependency.

For example, if it is a gaseous phase reaction, then I could choose temperature, pressure and mole fractions of all the components. And if I am dealing with mole fractions, we know that they all should add up to 1. So, we have mole fractions of only N minus 1 component, that is our reaction has N component let us say, or to be specific, let us say it has three components, then we need to specify mole fractions of only two components,

because, the third one will be determined by the fact that y 1 plus y 2 plus y 3 are all mole fractions should add up to 1.

In other words, if we have N components, we need only N minus 1, mole fractions. If you do not like mole fractions and we want to deal with concentrations for example, we could choose rate to express rate as a function of temperature, pressure and concentrations of N minus 1 species, once again N minus 1 because, when it comes to looking at concentrations, we know that there is an equation of state for gaseous components, which will relate temperature, pressure and total concentration.

Simply, put P V equal to N r T, and our concentration is nothing but N by V. So, there is a relation which defines the total concentration. So, we can choose any N minus 1 component, the other one is automatically fixed; or if you do not like even then, we could simply choose rate as a function of temperature and concentrations of all ==all== the components. So, pressure does not explicitly appear now, because that is now inbuilt in the form of expressing concentrations for all N species.

It is this last form, which is quite ==quite== common, particularly for reactions involving liquid solutions for gases, the first expression is more common either in terms of mole fractions or partial pressures, because if you look at partial pressure is nothing but, mole fraction into total pressure, so any one of those forms. But, if you look at any ==any== of these expressions, the total quantities that appear are N plus 1, that is N is the number of components plus 1. So, it could be either T P plus N minus 1, so 2 plus N minus 1 again N plus 1 and so on.

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Reaction rate – power law kinetics

➤ Consider a reaction $\Sigma\, v_j A_j = 0$ taking place in a closed, isothermal, constant pressure system

$$r = kC_1^{q_1} C_2^{q_2} \ldots C_N^{q_N} = k\prod_{j=1}^{N} C_j^{q_j}$$

q_j is the order of the reaction wrt species A_j
$q = \Sigma\, q_j$ is the overall order

So, now let us let us look at some of the common forms of these rate expressions and the most common form is the power law kinetics, so let us look at the most common form of reaction rate expression namely, the power law kinetics. Now, what is power law kinetics? Power law kinetics is simply put rate is proportional to concentration of species 1 to the power q 1 concentration of species 2 to the power q 2. So, products of all the, such C 1 raise to q 1 C 2 raise to q 2, up to C N raise to raise to q n.

In a compact form, we can express this as rate equal to K, K is that proportionality constant, product of C j rise to q j, j going from 1 to N. So, q j is the order of the reaction with respect to species A j; and this is the simplest form of form of power law power law kinetics. Now, we call this q j as order with respect to A j and if you sum up all these q j s, we get q, what we call as overall overall order.

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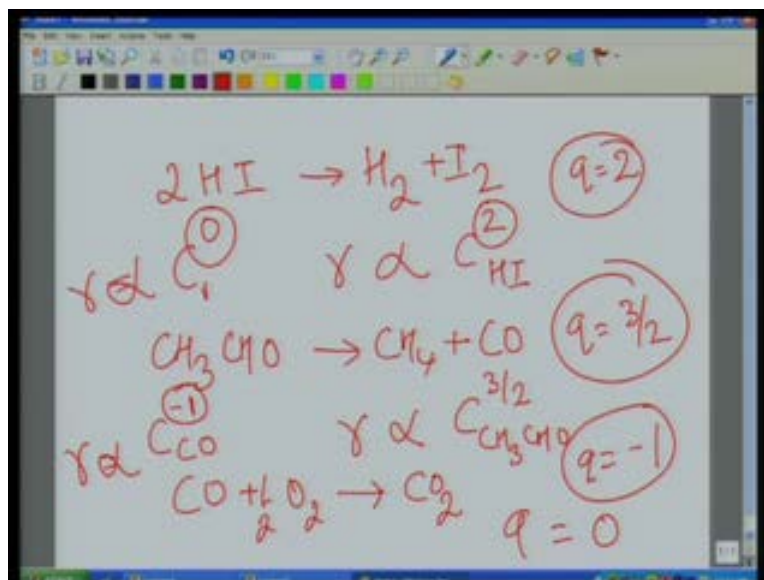
Let us take few examples and see what are the various possible orders that are that are possible, so what are the values of q that we can we can have? So, let us let us take few examples. Let us say, that we have a reaction of let me make it little darker, so we have a reaction of hydrogen iodide getting decomposed to H 2 plus I 2. Now, it turns out for this particular reaction, the rate of reaction is proportional to concentration of hydrogen iodide raise to power 2.

So, clearly in this case, q is 2 there is only one species in the reactant side, so our q j and q r q r are same. So, this is the this is the order of the reaction, so q can be integer. Let us take another example, decomposition of acetaldehyde to give us methane and carbon monoxide. Now, it turns out the rate of these reactions is proportional to concentration of acetaldehyde raise to power 3 by 2. So, q in this case is 3 by 2, or in other words, orders can be integers, they can be even fractions.

Do they have to be positive numbers? Not necessarily, for example, if you look at the reactions such as oxidation of carbon monoxide to carbon dioxide under certain conditions, for this reaction, the rate is proportional to concentration of carbon monoxide raise to minus 1 or in other words, the order now is q is minus 1, that is it can be negative numbers. So, the point that I am trying to make is, q can take any value, quite common to have positive numbers.

But, also there are cases, where q can be negative. In fact, quite often the power law kinetics is actually something which is fitted to the observed rate of reaction and when you do any numerical fit, there is no guarantee that q can be only in integers or positive numbers, negative numbers and so on. So, q can take essentially any of these values, that is positive number, integers, fractions, negative numbers or even 0; that is, if rate is proportional or rate is proportional to concentration of a species raise to power 0, so q can be 0. What it means is that, rate is actually independent of concentration. There are few real cases we will see examples of few of them, that under certain conditions, the rate is actually independent of <mark>independent of</mark> concentration.

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So, the order of reaction actually, let us revisit order of reaction, what is order of reaction? Now, if you say that I am going to define, I am going to just do it with respect to <mark>respect to</mark> two species because, same thing can be said with respect to any more number of species. So, if I say that my C 2 raise to q 1, C 1 raise to q 1, C 2 raise to q 2, I can write this by taking natural log, let us say of both sides as ln r equal to ln K plus q 1 ln C 1 plus q 2 ln C 2.

So, in other words, I can write my rate expression by taking logarithm of both sides, left hand side and right hand side and now, if you look at these expressions, I can write q 1 is nothing but, del ln r del ln C 1 or in other words, my q 1 is the differential of ln r with respect to ln C 1. Now, for true power law kinetics, this is what I get.

Now, there are quite often situations, where my rate is actually not power law kinetics, but something which looks of this type, that is when I have I have some complicated function K a C 1 C 2 divided by 1 plus K 1 C 1 plus K 2 C 2 and so on. Even for these cases, I can define my apparent order or observed order with respect to C 1, with respect to C 2, how do I do that? I know for my exact power law kinetics, definition of order is this (Refer Slide Time: 14:12).

That is, q 1 is ln r, del ln r del ln C 1. So, for any other rate of reaction such as this, I can take ln r. I can take derivative of ln r with respect to ln C 1. This is then defines If I do that for this particular particular function, what is this del ln r by del ln C 1? It is also nothing but, C 1 by r del r by del C 1, that is my definition of del ln r by del C 1, ln C 1. So, I can I can then take derivative, for example of this particular rate function and then, with respect to C 1 and whatever normalize it by C 1 by r, I will get apparent order with respect to species C 1, I will get apparent order with respect to C 2, if I do the same exercise with respect to C 2, that is C 2 by r del r del C 2. So, these are all what are called as apparent rates of rates of reactions.

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Now, this is as far as the as far as the rate power law, simple power law kinetics is concerned, a specialized case of power law kinetics is what is called as law of mass action, mass action kinetics. This mass action kinetics or law of mass action kinetics is again a case where, these orders are related to stoichiometry of the reaction. So, for

example, if q j is half of difference between mod nu j and nu j, then, we say we are the reaction follows law of mass action, mass action kinetics. To give you an example and this is this is just an example illustration, not real real kinetics.

For example, going back to our methanol synthesis, if we have reaction such as C O plus 2 H 2 gives rise to C H 3 O H, our general power law kinetics can be rate equal to K, some kinetic rate constant, concentration of C O raise to q 1, concentration of H 2 raise to q 2. And in general, concentration of methanol raise to q 3, some impaling the species 1, 2 and 3. So, what we have is, general power law kinetics, this particular representation for this reaction. What is our nu 1? Nu 1 for this case is minus 1, nu 2 is minus 2 and nu 3 is plus 1. So, if q 1, according to this formulation, is half of mod of minus 1 minus 1, there is a mistake. This should have been plus, yes. So, that would give us q 1 is 1; then similar thing would give q 2 is 2 and q 3 is 0.

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So, if that is the case, then our kinetics would simply look like kinetics will simply look like rate equal to rate equal to K into concentration of C O raise to 1, concentration of H 2 raise to 2, or in other words, the order and molecularity are same, and that is what is the law of law of mass action mass action kinetics.

Let me let me repeat that, let me repeat that in law of mass action kinetics, the orders are same as same as the stoichiometric coefficients or corresponding corresponding nu j and if for product, it is it is it is 0. I think I should stand corrected, what I had written earlier

was was the right one; that is q 1 is half of mod minus 1 minus minus 1, so that is 1. Similarly, we will get q 2 as 2 and q 3, that is, any any any product term will have no no influence on the rate of reaction. So, this is our law of mass action, mass action kinetics.

Now, let us look at how rate of reaction depends upon the temperature. Now, in earlier slide, we said that there is a rate constant K and it is a common practice to express rate constant K as a function of function of temperature. In fact, our earlier discussion on thermodynamics also told us that equilibrium constant also depends on temperature and for certain reactions, equilibrium constant will also appear in our in our kinetics and that also then, becomes the rate function of function of temperature.

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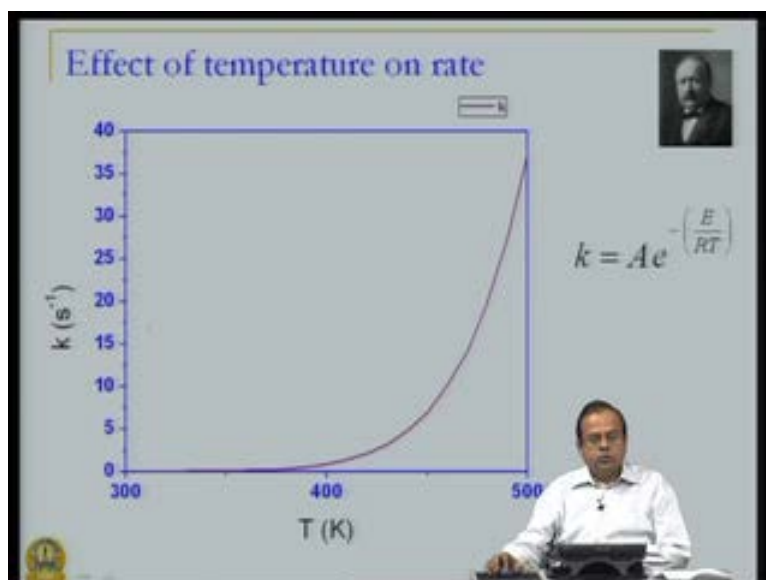
Now, a dependency of a rate constant on temperature was initially observed and an expression for this observation was provided by Arrhenius way back in 17th century. And what experimentally people had observed even before Arrhenius gave this mathematical expression was that rate constant, so what we are seeing here is the rate constant on y axis as a function of function of temperature. And rate constant increases as temperature is increased and in fact, increase is exponential in nature.

Arrhenius by using the arguments of activation energy proposed that, this relationship can be can be expressed in the form of K equal to A e raise to minus E by R T, that is that is a, the rate constant is rate constant K, is the frequency factor a exponential minus

e is the activation energy by R T R universal gas constant T as temperature. Now, what was <mark>what was</mark> his idea in <mark>idea in</mark> proposing this kind of rate expression?

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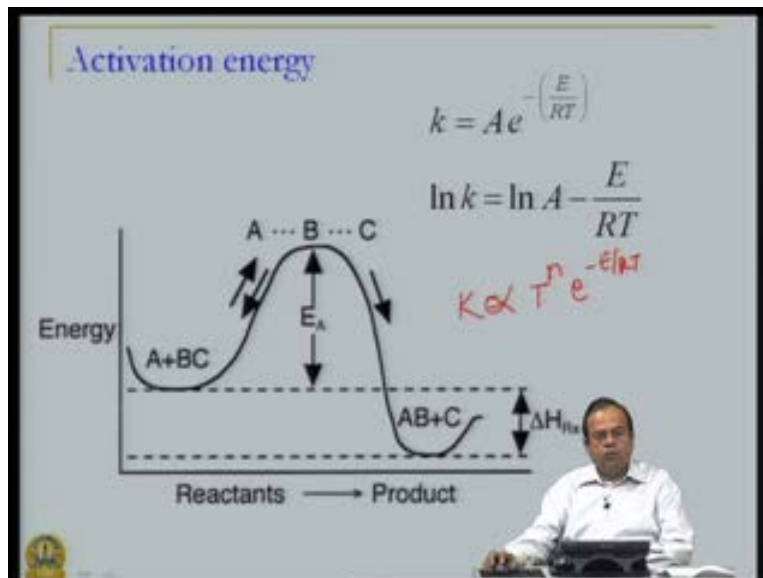
He argued that, if we have, let us say, a reaction <mark>a reaction</mark> of the kind that A goes to, <mark>let us</mark> let us say, A plus, B C goes to A B plus C, that is, just an hypothetical <mark>hypothetical</mark> reaction and so, if we now monitor or follow what happens to the energy of the system as the reaction proceeds. Reaction is proceeding from the reactant side to the product sides. So, x axis is representing the progress of reaction, y axis is representing the energy levels.

So, at the beginning of the reaction, we have reactants A and B C at certain energy levels. At the end of the reaction, we have products A B plus B C and for these reactants to go from A and B C to A B plus C, some energy barrier has to be overcome. There are various people have given various <mark>ah</mark> explanations. For example, <mark>ah</mark> complex a transition complex such as A B C is form from A B, A plus B C and then, this complex breaks down to give you A B plus C and information of this complex, an energy barrier has to be crossed, barrier of the magnitude E A or the activation energy and unless this barrier is crossed, the reaction cannot proceed; and hence the rate of reaction is dependent on temperature, in this particular <mark>particular</mark> manner. That is his idea. <mark>The</mark> <mark>that</mark> <mark>is the idea</mark> There are various other theories of slight modification, but this was Arrhenius, when initially he proposed, it is a purely empirical <mark>empirical</mark> relationship.

Now, there is a transition state theory, collision theory and so on, where the dependency is slightly different, in fact, in a more generalized form, the dependency can be written. That is, K is proportional or rather proportional to T raise to power, let us say, n T raise to power n, e raise to minus E by R T, where n can be 0 1 half, depending on what framework 1 is developing for, looking at the activation energy.

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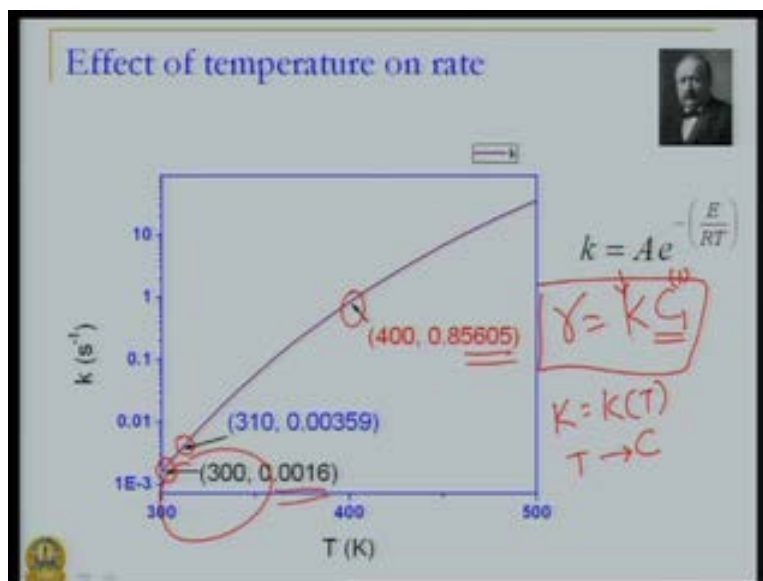
But, I want to point out, another interesting interesting aspect, that, what an exponential rate actually implies. Now, the same same information that we saw earlier, that this K increases exponentially as we increase the temperature. Let us put it put it slightly slightly differently, let me expand the scale or rather, let me make y axis natural log, to actually see what is what is happening here. So, what we see here is for example, when temperature is 300, I have used certain activation energy, the rate constant is 1.6 into 10 raise to minus 3. So, this is my rate constant.

If I increase temperature by 10 degrees, that means, close to 3 percent increase in temperature, what happens to my my rate constant? Rate constant is also also increases, but the increase is not as dramatic, let us say, from 300 to 310, the rate constant becomes 0.0035. But, let us see what happens if I increase my temperature by 100, that is 33 percent. So, increase in temperature is only 33 percent, but, look at what has happened to my rate constant.

The increase is now 2 orders of magnitude or 100 times and this difference go on widening, as we increase the temperature, or in other words, because this temperature dependency for rate constant is exponential form, it is a highly non-linear dependency; that is, small increase tends leads to a large increase in rate constant, which if we come in these domain, we can see from here to here, the rate constant has increased significantly.

Now, why is this crucial? This is crucial because, when you are operating reactors, and let us say that, you are designed everything to operate in temperatures in this range, for some reason, your temperature controller fails, temperature starts increasing. The temperature increase may not be dramatic; it may be 10 percent or 20 percent. The rates of reaction increases quite dramatically, 2 orders of magnitude for for less than 1 order of magnitude increase in temperature or in other words, there is a significant increase in rate of reaction and you never know what will happen if rate of reaction goes uncontrolled.

So, this is why, control of temperatures is crucial, but this also illustrates another aspect that, in design of reactors, when we are dealing with kinetics, even for first order kinetics or when q is q is 1 the order, we could have significant non-linear behavior, because of temperature variation in the system. Let me reiterate, if I say my rate constant rate of reaction is K C 1 raise to 1.

So, a first order reaction, we all know that first order reaction implies linearity of rate and concentration. However, even though rate and concentration are linear, as it appears in this expression, the rate constant K is dependent on temperature in a non-linear manner, such as shown over here. Now, as we will see later on, in a reactor, concentrations and temperatures do not change independent of each other; at least if you are talking about, let us say, adiabatic reactor. So, if we are talking about adiabatic reactor, and let us say exothermic reaction, then, concentrations and temperature are related to each other.

So, in other words, even though the kinetics is first order as it appears, there is a indirect influence of concentration on the rate of reaction. Direct influence is through this C 1 over here; indirect is because K depends on temperature and temperature is related to concentration. So, this indirect effect is felt here. So, even for simple first order kinetics, we could have dramatic effects in terms of how reactor behaves.

We will see those examples, but origin of those effects can be seen even for simple reactions reactions like this. Now, coming back to our activation energy complex, if we say that, this is a barrier, higher is the barrier, higher will be higher is the barrier lower higher will be the energy that will be required, and lower will be the rate constants.

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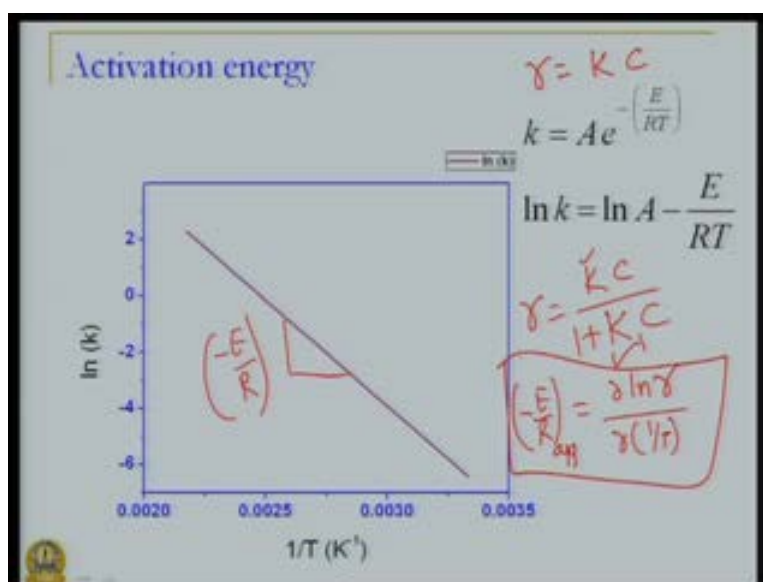
What is activation energy? If we mathematically look at the expression for k, k is A e raise to minus E by R T. So, ln k is ln a minus E by R T and if you plot ln k versus 1 over T, the slope of the line is given in the form of form of slope of the line gives us the activation energy.

So, this slope is now nothing, but E by R, just as we talked about apparent order, when we talked about reaction rates, which do not necessarily follow power law kinetics. But, we can define apparent order as ln r partial of ln r with respect to ln C 1. We can also define the activation energy or rather apparent activation energy, when r does not necessarily follow simple simple power law kinetics.

For example, if you have a rate expression which looks something like this K some kinetic rate constant times concentration divided by 1 plus some equilibrium constant K 1 into C, we will see where those equilibrium constant is coming and this is where I said, there there is a possibility that equilibrium constants also appear, this actually appears for a lot of gas-solid catalytic reactions.

So, if you have something like this, then we know k is a function of temperature capital K 1 or this equilibrium constant is also function of temperature. So, there is nothing like single activation energy even, both of these are function of temperature. But, we can define apparent activation energy or apparent activation energy or minus E by R and what will that be? Recalling the same exercise that we did for apparent order, it is now del ln K or ln K or ln r divided by del of 1 over T.

So, we can define, we can define now we can define recall that r is K into C. So, if this was my kinetics, del ln K del 1 over T would be same as del ln r del 1 over T because, ln r is nothing, but ln K plus ln C.

So, derivative with respect 1 over temperature of r and K will be same, and this is what is used in finding, the apparent activation activation energy. Why these apparent order apparent activation energies are are required? As we will see later on, not just for this kind of reactions; but reactions where transport is important, we find that rate of reaction actually may not be given by the kinetic rate expression such as this. But it may involve transport processes, diffusions, mass transfer rate. So, rate of the the rate may may be actually govern by the diffusion rate, for example. Now, diffusion rate dependency of diffusion rate processes on temperature is much milder than the dependency of kinetic rate constants on temperature. Kinetic rate constant on temperature is exponential, as we saw here.

So, what happens, when you take a derivative like this? You get an activation energy value, which is fairly low. In fact, if diffusion process is independent of temperature, then the activation energy or the apparent activation energy for such process would be 0. So, when it comes to making some judgment, whether processes are transport related or transport controlled or kinetically controlled, good rule of thumb is to look at the activation energies. And if activation energies, typically 40 kilo kilo calories per mole to 100 kilo calories per mole are typical of any chemical reaction. But, if values are much lower than that, that indicates that it is not the kinetics, but something else that may be controlling the controlling the process.

Let us now come to reversible reactions, that is, what we are saying is, we have a reaction, let us say, A 1 plus A 2 gives rise to A 3 plus A 4. So, we have now a reversible reaction and reaction can go from left hand side to right hand side or right hand side to left hand side and so, rate of these reactions are now involves components from the left hand side to right hand side of the reaction. We call this reaction as forward reactions.

So, this is my forward reaction and the, that is, left hand side to right hand side and this is my backward reaction, from right hand side to left hand side. So, I have rate, given as rate of forward reaction minus the rate of backward reaction, then, the total rate, because, there is something going from A 1 to A 2 that is forward, something going from A 3 to A 4, that is that is reverse.

We can express both forward reaction rates and backward reaction rates as power law kinetics and we have, for example, if you choose r f as product of C j raise to q j and the forward rate constant k f r b as product of C j raise to q j prime, need not be same as q j over here and the rate constant k b. So, the net rate of reaction is the product of C j raise to q j K f into that product minus k b into C j raise to q j prime.

Once again, law of mass action kinetics is a special case, where q j is half of mod nu j minus nu j and q j prime is half of mod nu j minus mod nu j plus nu j. If you take the same reactions, A 1 plus A 2 going to A 3 plus A 4, I can write for law of mass action kinetics, K f C 1 C 2 minus K backward C 3 C 4; and you take the generalized power law

kinetics q j q j prime, put the appropriate value of nu j, you will find that, this is what the rate we get. You get and this is, what is the law of mass action kinetics, for a reversible <mark>reversible</mark> reaction.

Now, there are several aspects of reversible reaction, that we should <mark>we should</mark> be worried about or concerned about. And let us go <mark>go</mark> to a specific example, to <mark>to</mark> see this particular aspect.

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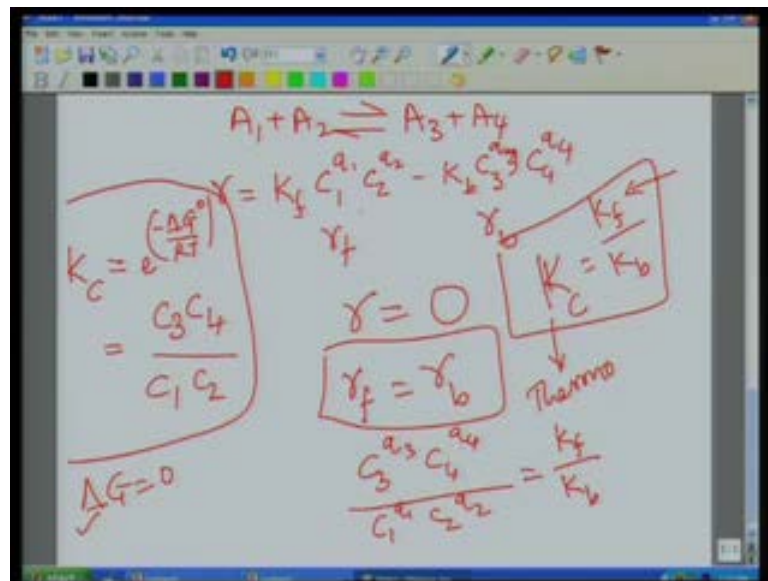
So, let us say that, we have our reaction A 1 plus A 2 giving rise to A 3 plus A 4. We wrote this reaction rate as r equal to K f and I am in general going to write C 1 raise to q 1, C 2 raise to q 2 minus K backward <mark>C 3 raise to q 4 and C 4</mark> C 3 raise to q 3 and C 4 raise to q 4.

We are considering the reversible reaction and we are interested in seeing what happens to these rates of reaction, as these reaction approaches equilibrium. If you recall, when we discussed about thermodynamics, we said the following and I want to bring that once again, <mark>that</mark> for this particular reaction, we will have the constant K C the equilibrium constant, which is e raise to minus delta G 0 by R T, delta G 0 a thermodynamic property, so given temperature, this K C is fixed which is nothing but, C 3 C 4 divided by C 1 C 2.

This is my true this is my true thermodynamics; this we saw in our last class. Let us visit that equilibrium in a slightly different manner. When this reaction is taking place, what happens? We have forward reaction rate which is this r f and we have reverse reaction rate which is this r b.

Now, when does when equilibrium is reached, the process simply comes to a halt, the net process comes to a halt. We also talked about what is actually happening, is at equilibrium. This forward rate of reaction is counter balanced by the reverse rate of reverse rate of reaction. So, if that is the case, then what is the rate at equilibrium? At equilibrium, rate must be then 0. So, the net rate is 0 or r f is equal to r b.

Now, if we take this kinetic kinetic interpretation of equilibrium, and I want to stress here, the condition of equilibrium is free energy change is 0. This is not the condition of equilibrium; this is a consequence of equilibrium. one often gets confused between what is the condition of equilibrium and when I normally ask this question in my class, I get 2 kinds of answers; one the correct one, which says that the free energy change must be 0 and one which is incorrect which says that rate of forward reaction is rate of backward reaction, it is incorrect in the sense, that the true condition is this, is a consequence. So, we cannot say that this is the condition of equilibrium.

So, if you have rate of forward reactions same as rate of reverse reaction, then if we put this, we get the following C 3 raise to q 3, C 4 raise to q 4 divided by C 1 raise to q 1, C 2 raise to q 2, because, this particular rate is equal to this particular rate. What is this equal to? This is equal to K forward divided by K backward.

Now, recall that K forward and K backward are kinetic rate constant. We know at equilibrium, the equilibrium constant maintains certain relationship between the concentrations. In this particular case, K 3 C C 3 C 4 divided by C 1 C 2. Since, both conditions, we are looking at same equilibrium, there has to be consistency between these two. For the For example, my equilibrium constant K f K C is now K f by K b. What does it imply? It implies the following that, if I have a reversible reaction, then I do not have freedom of choosing K f and K b arbitrarily. Whatever may be the value of K f and K b, the ratio of two must be the equilibrium constant, which is already predefined for me from thermodynamics. So, this is from thermodynamics.

So, if I estimate a value of K f, then my K b is automatically fixed, because, the ratio of two has to be equilibrium constant. So, I do not have that I do not have that freedom to choose K f and K b independently. I could choose K b independently, but then K f is fixed, so it is a it is a same same story.

Further, you look at these ratios, which is C 3 C 4 by C 1 plus C 2. So, q 1 q 2 q 3 q 4 are also not cannot be randomly chosen. For example, a simplest case we can we can choose is the following; let me remove all these things.

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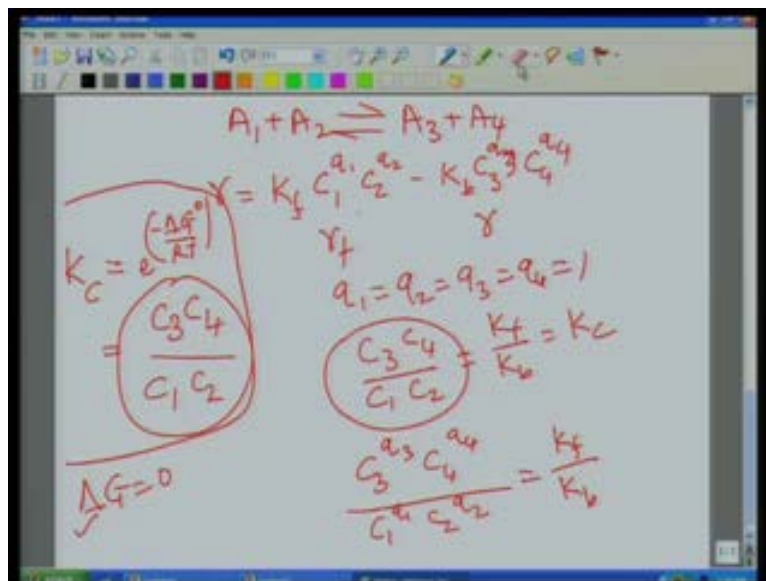
So, we can choose all all q 1 q 2 q 3 q 4 as unity and then, this will become C 3 C 4 divided by C 1 C 2, which is K f by K b, which is which is constant K C.

In fact, what it means is, I cannot have q 1 q 2, let us say 1, q 3 q 4 as 2. Because, that would mean that, this particular relationship is not consistent with our thermodynamic definition of equilibrium equilibrium constant. So, there is a restriction on how we can choose choose q 1 q 2 q 3 q 4. In fact, it turns out for a general power law kinetics, we can we can they need not be actually all unity.

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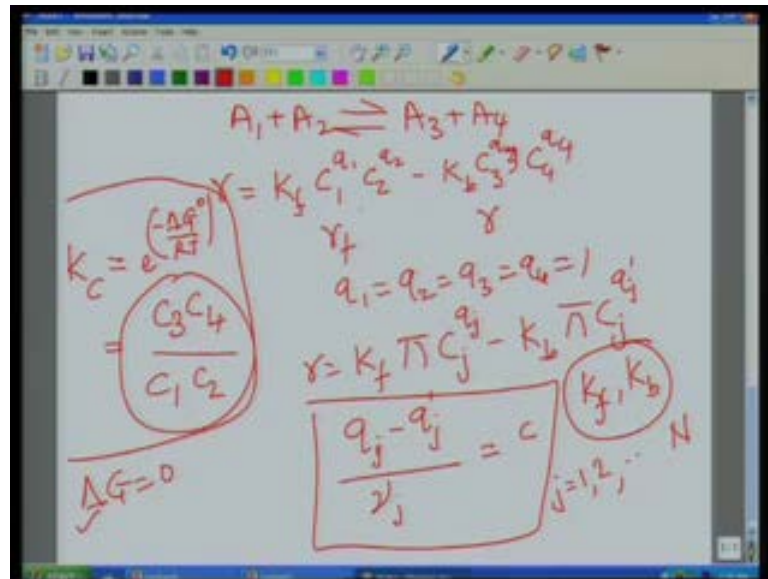
We can <mark>we can</mark> say that, as long as the ratio of so, for example, if I am defining my, as long as my ratio of q j by q j prime divided by the stoichiometric coefficient nu j, is some constant C, a non- 0 constant, but, this is same for all species. The thermodynamic consistency is <mark>is is</mark> followed.

So, we should ensure that, for a general reversible reaction, if we are framing power law kinetics of this kind, firstly, K f and K b cannot be independently chosen. Because, there is a thermodynamic restriction and secondly, the orders q j and q j prime also cannot be independently chosen, there is a restriction that q j minus q j prime divided by stoichiometric coefficient nu j has to be some constant, non zero constant, zero would not mean anything.

So, it can be 1 minus 1 half minus half, whatever you want, but, as long as it is same for all species, that is for species 1 2, up to all n species. As long as this ratio is constant, we are, we have not violating the thermodynamic consistency.

We will stop here for the day and look at how these rate changes, as the reaction proceeds, because, to have it, it is important to have some qualitative understanding of how rate of reaction changes as reaction <mark>reaction</mark> proceeds. So, this will be the topic of discussion for our next session. Thank you.