Fundamentals Of Combustion (Part 1)
Dr. D. P. Mishra
Department of Aerospace Engineering
Indian Institute of Technology, Kanpur

Lecture - 25
First order, Second order and Third-order reactions

Let us start this lecture with the third process from the Peter Atkins chemistry begins in the stars.

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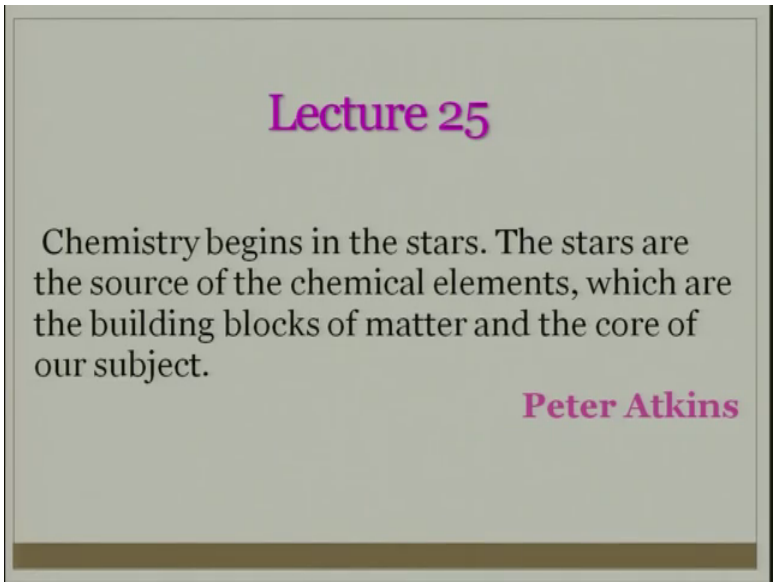

The stars are the source of the chemical elements, which are the building blocks of matter and the core of our subject. So, that is his belief, but of course, one can question it, that one um, let us, you know if you recall that in the last lecture. We talked about arenious form of reactions and then it is limitation. And keep in mind that you should not use that for a very long range of temperature; however, the temperature range is not too long. You can use it and we have seen how we can evaluate the activation energy provided. You know the specific reaction rate constant at two different temperature.

Generally, people use of course the several of temperature and then, put a curve fitting and then do that right. It is not that they will take two points and then calculate no first. They will calculate the data and then they will calculate what will be the activation energy provided. It is linear in nature and if it is not little bit deviation, they will make it linear. So, now, let us look at, you know elementary reactions.

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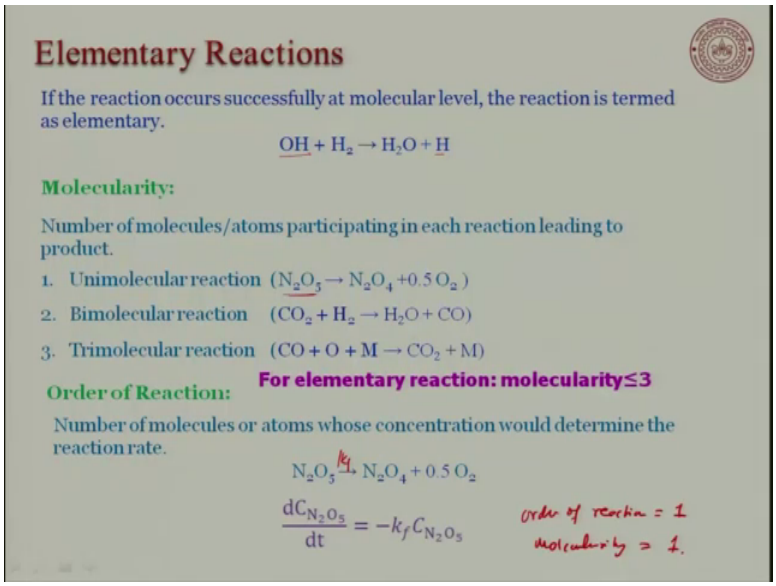

Because in case of elementary reactions, the reaction occurs at a molecular level right and we are taking an example O H is reacting with hydrogen and leading to water and H and keep in mind that H is a radical and O H also radical and we have seen that molecularity. We have discussed earlier, but I want to again discuss these things and, because, you know is important to learn, what is difference between the molecularity and the order of reaction.

So, in molecularity basically, number of molecules are atom that participate in each reaction leading to a product right and let us consider some of the you know, reactions, which is unimolecular and then like for example, N 2 O 5 is the composite, N 2 O 4 and oxygen, in this case, the reaction. The molecularity is for this reaction is only one that is why, we call it as a unimolecularity atom and bimolecular reactions, if you consider C O 2 is reacting with the hydrogen going to water and carbon monoxide, the two molecules are participating, leading to a product. So, therefore, we are calling it as a bimolecular, trimolecular of course, three molecule will be, reacting to getting into product right. In this case carbon monoxide is reacting with O, with third body, which is not participating, but; however, without that reaction may not occur and that is C O 2 plus M, right.

And keep in mind that for elementary reaction right, and these are, not really elementary reaction, this is the elementary reactions. For elementary reaction, what will be the, you know molecularity. For example, this is like, in this elementary reaction two molecules

are reacting. So, therefore, molecurity will be 2. So, can I have a, elementary reaction, where molecurity will be 5 or 4.

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So, generally it is not true. Generally, for elementary reaction molecurity will be always less than equal to 3 ok. Beyond that, it is not possible for elementary reaction whereas, for you know global reactions, which is hypothetical reactions that I mean theoretic, I mean like what we assume there, you can have right. So, whereas, order of reactions talk about the, you know will be different than the molecularity, because that will tell you that whether the reaction rate will be dependent on the concentration and the what is it is power right, coefficients right, power.

For example, if I consider this N 2 O 5 leading to N 2 O 4 and half O 2, in this case reaction rate. What it would be? It would be the, the change in concentrate N 2 O 5 divide by dt is equal to minus k f N 2 O 5, if I say this is your k f right that means. In this case, order of reaction will be one right, order of reaction right. Order of reaction will be 1 and molecularity is also 1 right. So, but molecularity need not to be order of reaction, for all the reaction, for you know reaction that might be, this is a one example, where it is looks to be same, but need not to be same all the time.

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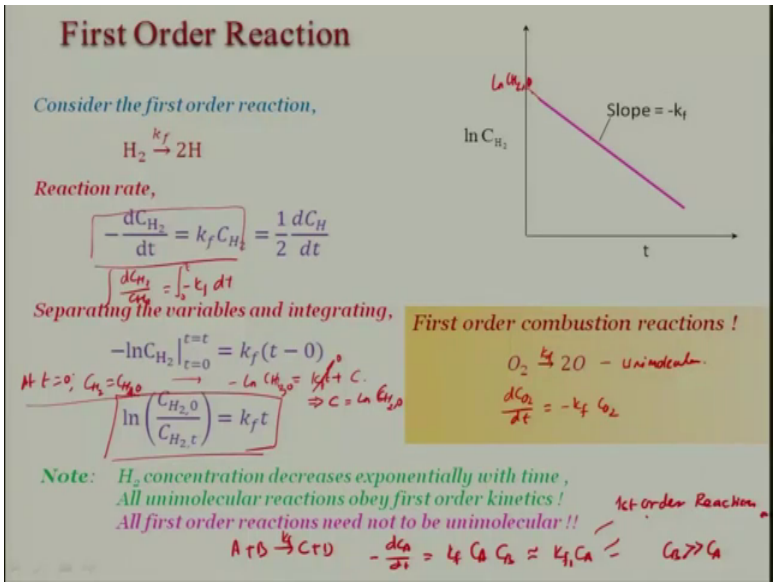

So, let us consider the first order reaction, as we have already seen that O 2 is reaction with 2 O right and in this case, the what will be BC, if I take BC O 2 by dt. If I say this is kf is equal to minus kf C O 2 right. So, this is basically first order reactions. So, similarly you can consider H 2 going into the 2 H, which is then the reaction rate will be dCH 2 divide by d, t is equal to kf dH 2 and that also you can write on equal to half dCH by dt right. And keep in mind, this is being consumed. Therefore, there is negative sign and BH is being produced therefore, this a positive sign right.

And if I consider this portion only right, what I can write down right, I can integrate that and separating the variable. I can write down dCH 2 by C H 2 is equal nothing, but kf dt and I will integrate this thing 0 to t time here, right ok. So, I will get ln CH, t is equal to 0 to t and kf t at, this thing then, I can, what you call, get a relationship ln CH 2 O divide by l n CH 2, kft keep in mind that plus there will be a constant right ok.

So, in this case, if you look at this will be minus ln C H 2 is equal t kft plus is equal to constant right, right at t is equal to 0, at t is equal to 0. What it will be CH 2 will be nothing, but CH 2 comma right at the initial state right. So, therefore, the constant is coming. So, if I will apply this one then this is nothing, but your CH 2 at this condition, this will be CH 2 O. So, and this will be t right, this will be t, t is nothing, but 0 right, at t is equal to 0. This I am talking about then simply C is equal to ln CH 2 at 0, this will be little capital right. So, from that, you can get ln CH 2 O divide by CH 2 at time t is equal to nothing, but kft right.

Now, if you plot this thing, you will get basically, slope that is the minus kf right and that time is equal to t, what is this value? This is nothing, but your corresponding to ln CH 2 naught at time t right and as it goes the time, this is being reduce kind of things. So, you can get basically, you know how does the hydrogen, you know concentration changing with respect to time, you can, find it out very easily, if it is a first order reaction keep in mind that in this case the hydrogen concentration decreases exponentially with time.

Of course, this is plot in ln, but if I plot CH 2. So, it will be very clear, it will be exponentially. You know, changing or decreasing with time. All unimolecular reactions obey the first order kinetics right. For example, this a unimolecular oxygen going to the O 2 right. This is a unimolecular reaction.

But all first order reaction need not to be unimolecular there might be a two molecules will be participating, but; however, there might be a situation where some, reaction will be first order in nature right. So, now, and that will be occurring particularly, when the one molecule concentration is too large to be changing with respect to time then you can have for example, if I say A is reacting with B going to C plus D right.

If I say, this is kf I can write down dCA by dt minus is equal to kf CA and CB right. So, if CB is too large right, it is not really changing with respect to time, then this will be nothing, but your kf right of course, this will be, you know CA. So, although this is basically, kind of 2 molecules are there and then this will be, but it will be only constant with kf 1 I can say.

So, therefore, this is A and that is possible will be CB is very-very greater than CA. So, therefore, it will be unimolecuar reaction. In this case molecular rate is, what basically two right, but; however, the order of reaction is 1 order of reaction will be 1, first order reaction, but the molecularity in this case is 2.

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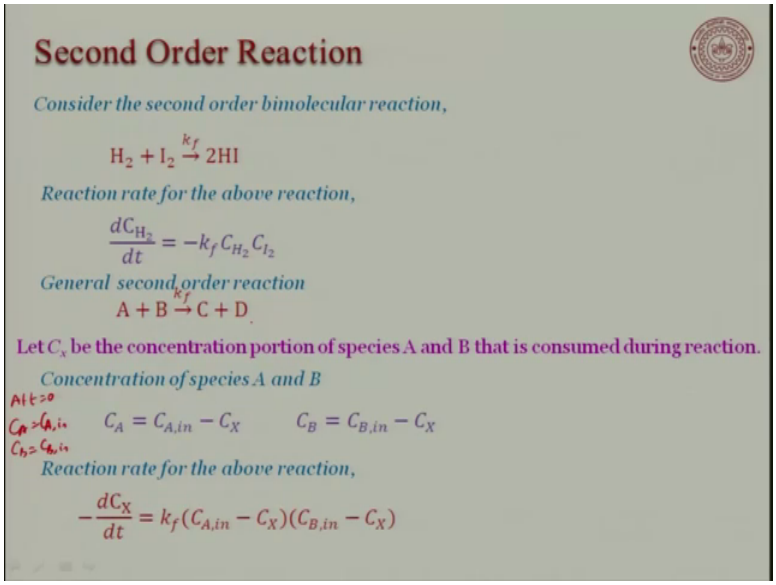

So, now let us look at second order reactions right, let us say that hydrogen is reacting with a iodine and going to hydrogen iodide 2, hydrogen iodide and reaction rate, if you look at this, is nothing, but dCH 2 dt is equal to minus kf CH 2 CI 2 and if I write down general second order reaction, we can look at A plus B going to the C and D with reaction rate. You know specific reaction kf, this is a forward reaction. So, concentration

of species right so, if you look at this, this is basically reaction rate will be dCA by dt minus will be kf CA CB right.

Let us assume that CX, you know is the things, which is changing with respect to time of the concentration of A and B then CA of concentration will be C at initial. When Ca is basically at t is equal to 0 CA will be CA initial right and similarly, CB will be CB initial and then that is CB will be CBin minus CX. CX is what the concentration, which is changing with respect to time right and that CB is, CA is basically a CA initial minus CX.

All the time Cx is changing right, but CA is initial constant, then CA is basically changing with respect to time and keep in mind here, we are considering for the simplicity, say that both CA and CB is changing with the same concentration, but need not be true all the case right, but in this case, we are taking, because to make it little simplify, the thing reaction rate, above this constant will be dCX by dt right is nothing, but your D dai in minus CX into kb dcx by this thing right, because we are saying that how it changing like this is nothing, but if you look at this is I can write down as X right changing.

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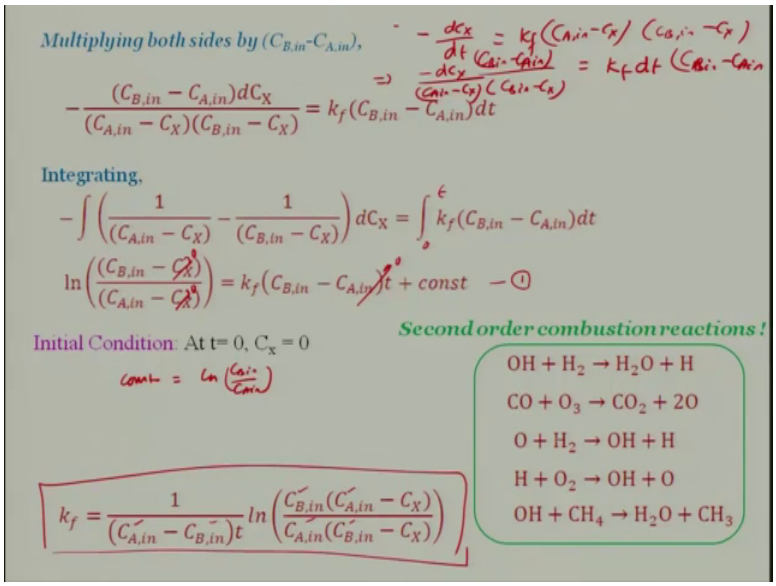

Now, what we will do? We will basically, multiply that thing with the both the sides, CB into minus CA 1 right. So, if you look at earlier, we had seen that, minus dCX by dt is equal to kf CA in minus, CX into CB in minus CX right minus dC X divided by CAin

minus CX into CB in minus CX is equal to kf dt and then in here, I will multiply it by C CB in minus CA i in and in this side also I will multiply it as CB in minus CA in right.

For both the side; left hand, right hand side, I am multiplying that is nothing, but this one now, this case I can write down as, as what can I write down here? I can write down as 1 by CA in minus CX minus 1 by CB in minus CX right of course, there will be minus sign here dCX is equal to kf CB in minus CA in into dt, right. Yes or no.

So, then I will integrate it, if I will integrate this thing, I will get this integrating, for thing and this is basically 0 to t I can write down right. So, initial condition, if you look at at t is equal to 0 what will be CX? CX will be 0 is not it, because there is no change in the concentration right of that. So, right at t is equal to 0 CX will be 0 and then if it is 0, this thing what I, what I will be getting? This will be at t is equal to 0, this will be 0 right and, this will be 0, this will be 0 right.

So, I can get basically, in this case what I will get, I will get ln right, constant is equal to ln CB in by CAin right is not it that I will get, because this constant, this is 0. This is 0, that is nothing, but ln B. So, if I substitute over this and this constant, this equation, let say this is equation 1 right, then I will get kf as is equal to 1 over CA in minus CB in t right. This portion is ln, this portion right into CBIN divide by CA in.

So, this I will get a expression right and of course, these are all known CB in I, all are known and CX, if I know this concentration I can measure with respect to time then I can find out, you know what will be, how this, you know kf right. So, by this you can find out, the, relationship for the kf with respect to C and if I know this kf, you can also find out how this CX will be vary with respect to time right.

So, there are several you know second order, combustion reaction, which will be taking place in the elementary level, if you will look at like these are the reaction O H reacting with the hydrogen, getting into water and H atom and C O plus ozone, you getting into CO 2 and 2 O and O is reacting with hydrogen, getting into OH plus H and H is reacting with O 2 getting into O H plus O and of course, this O H is reacting with methane getting into water and CH 3 of course, some of the examples I have given here.

There might be several of them, which will be you know, there in that case. So, let us now look at the third order reactions.

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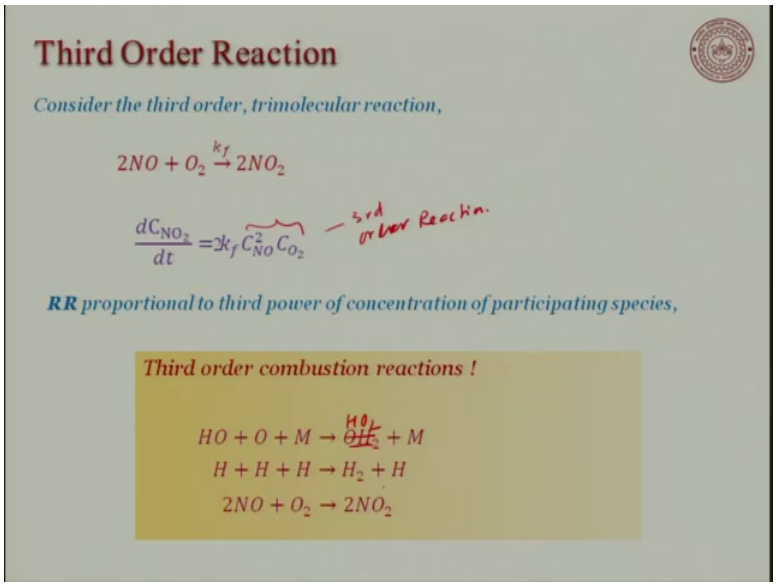

So, let us consider the third order reaction, which is trimolecular reactions, right. 2 N O is reacting with oxygen, getting with 2 N O 2. This we are already discussed. So, if you, write down this reaction is basically 2 C NO 2 dt is equal to 2 kf right, CNO 2 and C O 2 right, because this is being formed therefore, there is no negative sign and this reaction rate, keep in mind that this is proportional to right, third power of concentration right, of the participating species. Therefore, this is the third order reaction right, because this is 2 index and this is 1.

So, basically 2 so, therefore, and third order combustion reactions, some of the examples, I have shown here that is H O, reacting with O getting in and also with a third body and became O H 2 plus M H O plus O H O 2 ok. This will be H O 2 plus M and H 3 H is reacting getting into hydrogen plus H right 2 N O reacting with O 2, getting into 2 N O 2 right.

So, these are the third order reaction, what will be, considering and in the next lecture what will be discussing? Will be basically discussing about the reverse reaction and how to handle those things, and later on will be looking at the chain reactions right. So, with this we will stop over here.

Thank you very much.