Fundamentals Of Combustion (Part I)
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Lecture – 20
Lecture 20 Compact notation and reaction rate of chemical reaction

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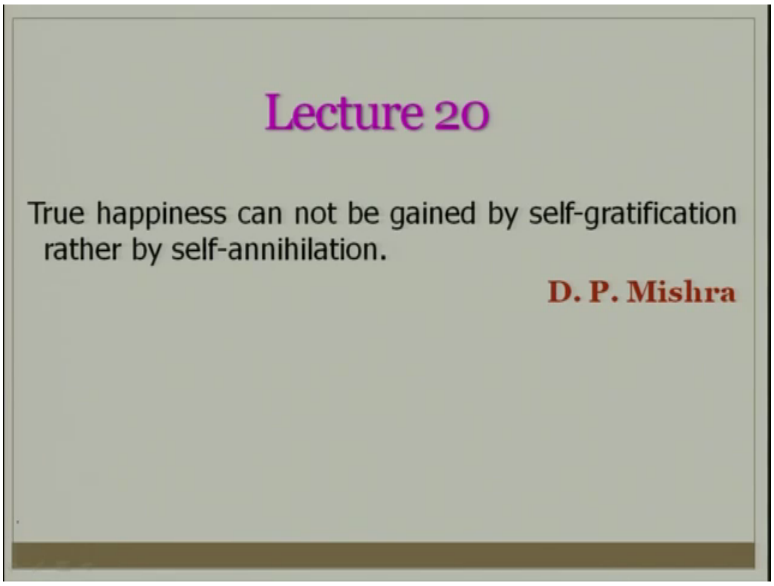

Let us start this lecture with a thought process true happiness can not be gained by self-gratification rather by self-annihilation. That was thing what was followed in our country may be 100 years back, but today with the market forces we are doing gratification ok. So, let us now get back to what we learned in the last lecture we basically looked at the reaction kinetics right, and we also recall how we used the law of mass action?

And in the end I talked about little bit how we will invoke the collision theory to evaluate the specific reaction rate, but what we will do today we will now look at little you know way of how to represent this thing compactly and then we will move what some kind of elementary reaction, then we will go back to the collision theory ok.

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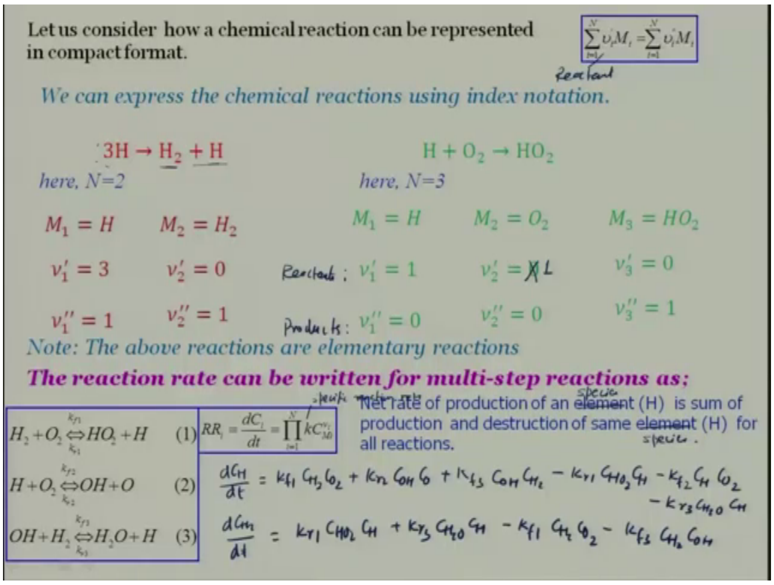

So, let us consider; how a chemical reaction can be represented in compact form right. You might be wondering, why I need to have that? This is a thing which was not very important may be something 30 – 40 years back right to represent write the chemical reaction in a compact way. So, let us see that we can do that in a very compact mathematical form into nu i M i nu i dash you keep in mind this dash. Summation over all the participating species i is equal to N and this is of course, the product side i is equal to 1 to summation of all nu i double dash M i. So, what is the meaning of that? Is we will explore it will further, because if you look at it will looks to be little complex. So, let us consider a you know.

Chemical reaction and for expressing it in terms of index notation for example, if I say 3 H going to the H 2 plus H; that means, in this case how many participating species are there H and H 2; that means, 2. So, if you look at this N right this will be how many it will be 2 rights. So, that will be will be 2.

Now, I want to write in a very compact way. So, if you look at it is written in a very simple way 3 H H 2 plus H, if I want to write in more compact way; what I will have to do like M 1 is nothing, but your H right, because M 1 and M 2, there are total if I look at this portion first I am looking at right like this is your reactant this portion is reactant.

So; that means, if I will consider this M 1 H nu 1 dash will be definitely 3 and what will be nu 2 dash? 0 because there is nothing; no hydrogen here in the left hand side the reactant side right the reactant side there is no hydrogen right. So, therefore, because M 2 is present in the H 2 and in the product side like if you look at this is hydrogen 1 H atom under product side therefore, nu 1 double dash is equal to 1 and 1 hydrogen molecule on the product side therefore, nu 2 double dash is equal to 1; is that clear? Not getting, it looks to me see; what I am saying?

I am just writing in a compact way right question might be coming to your mind; why I will do that? you think about why we want to do? In a writing it is a very simple way, I can write right; let us taken another example right where you you will tell me like what is this N here; N is equal to capital N is equal to 3, H O 2 H O 2 right ok. So, now, if I will write down in this compact format, then what I will have to do? I will have to write in this way M 1 is equal to H M 2 is equal to O 2 and M 3 is H O 2 right.

Now, is it right whatever nu 1 dash H for the reactant, this is for reactant right. This is the product side right is it right or is it wrong is not right ok. So, what is that nu 2? If you look at O 2 it is here O 2. So, therefore, this will be wrong this will be 1; yes or no rest of the things is right are you getting? Yes or no.

Student: yes

So, you know why we will right in a such complicated way, because we want to you know stimulate the kinetics for that computer wont understand this way computer understand in a compact mathematical form; where you will be recognizing this species M 1, M 2, M 3 like that; you know it will be are you getting? So, for computer it is required, but earlier days it was not. Now we will have to coding other things and then of course, I will see whether I will get into otherwise if you want to you will have to get into matrix format you know this will be easier to do that; that is why it is being done.

I am just introducing, but it is not very important right. So, that you can really at least aware that yes; it can be written in this format. Now, above reactions are elementary reactions right. So, it will be generally use for elementary reaction, because when you look at some kinetics right we always try to you know do use the elementary reaction, but that does not mean we won’t be using global reaction right can it we will be using, but this is more predetermining.

Nowadays particularly with the increasing the computational power people are going for better kinetics or stimulation. So, now, this is of course, you are writing, but now if you want to right reaction rate you know in a multi step chemistry and there are several reactions which are taking place let me let us take some example right which can be written in a very complex format right which we have already aware; that is reaction rate of ith species is summation of k; k is your specific reaction rate right is not it and C is the concentration of M i.

M i is this all this species whatever represented and nu i right. Now I will take 3 reactions: H 2 is reacting with O 2 going to H O 2 ad H keep in mind these are elementary reaction there will be forward reaction k f 1 and there will be backward reaction k r 1, that is reverse reaction right. Reaction rate these are reaction rate the you know co-efficient or specific reaction rate whatever you call right.

Similarly H O 2 k f 2 O H plus O and of course, there is a forward reaction the you know co reaction rate coefficient have written and k r 2 is the reverse. Similarly O H H 2 going to the H 2 O and H. Now I want to find out right; what will be the reaction rate for H? Let us say we will do that right; how we are going to do? For any species I want to do for all this three reaction, because if you look at here the H is being produced right.

In this case H being also produced and also getting conjured in the reaction 1 H is produced and also being conjured you know for what reverse ok. And similarly in reaction rate 3 H is being produced, and also this thing right , but if I consider hydrogen only in the reaction 1 and reaction 3 right and in the reaction 2 the hydrogen is not there. Yes or no. Now I want to write down I will have to do in a systematic manner right. So, for that net rate of production of an element for example, H or hydrogen right or species rather I could have put it here species not.

Element species is the better one. Species mean it can be element it can be you know molecule it can be anything species right. Now, if I will right down let us write down for C H as I have told for this thing here ok. So, what it would be d C H by d t; I can write down this is being produced. So, k f 1 C H 2 C O 2 yes or no right; I will be talking about first is production right of H.

So, then what I will do I will get into the reaction 2, H is being produced if you go in a reverse direction otherwise no so, then what will be that k r 2 C O H C O; yes or no. Yes or no right and here in this case the reaction 3, the H is produced in the forward direction. So, this will be k f 3 C O H and C H 2 this about being produced and it is also getting destroyed. So, we will do in a systematic manner. Now H is being destroyed right H is destroyed means, how it is destroyed in the reverse direction?

So, I will write down minus, because destroyed right and k r 1 C H O 2 and C H yes or no; right and similar way if you look at the distraction in this reaction 2 right it is in the forward direction. So, I will write down k f C H C O 2 minus; so this is 2 right and this is taking place in the reverse direction. So, this will be k r 3 C H 2 O C H; yes or no right.

So, just to make you familiarize you know let me consider another this thing example I mean how to write it down this C H 2 by d t will be if you look at this H 2 is being produced in the reverse way. So, therefore, what I will write down? I will write down k r 1 C H O 2 C H right. And in reaction 2 hydrogen is not there.

So, therefore, we won't consider and in this case in the reaction 3 the hydrogen is being produced in the reverse direction right. So, I can write down k r 3 C H 2 O C H, then I will have to look at distraction H 2 in the forward direction. So, therefore, I can write down k f 1 C H 2 C O 2 and in the reaction 3 the H 2 being destroyed in the forward direction.

So, minus k f 3 H 2 C O H yes or no. So, now, this reaction you know if you look at it will be if you use this compact scheme it can be written in a matrix format and the reaction rate you can substitute and then add together all those things can be done very easily. I am not going to show that, because it will be little complex and we wont be using in our this course, but whenever you are doing some kind of a programming and then stimulating the things for stimulation of the reacting flow, then you need to look at it.

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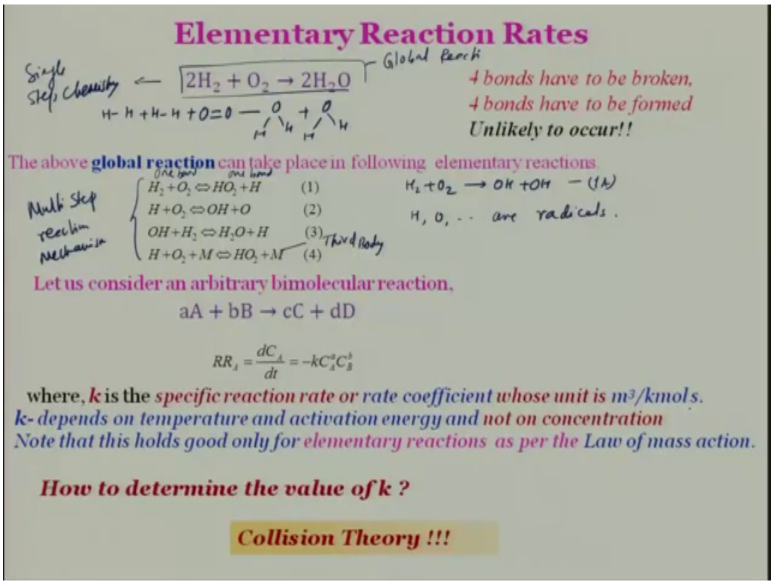

So, let us now get into the elementary reaction rates, what we are considering? I will just develop an; what I had also discuss? Let us consider a two moles of hydrogen reacting with 1 mole of oxygen going to the product of two moles of water right and this is if you look at what is happening here? If you look in terms of breaking up bonds and forming up bonds in this case right; how many bonds are being formed in broken?

The reactant side it is nothing, but H right plus H H right plus this is O double bond right minus O H H plus O H H right so; that means, total in reactant side four bonds are being broken and in the product side total our bonds are been broken which is one hydrogen molecule on the product side therefore, nu 2 double dash is equal to 1; 1 hydrogen molecule on the product side therefore, nu 2 double dash is equal to 1 (Refer Time: 15:45) single step chemistry right away.

We do use single step chemistry particularly in the stubborn application or ic engine you know people do use for that, because that is very complex right. We use a you know global reaction for modeling the flow provided your computational capabilities is very very small and also you want to get answer quickly right, but; however, with the modern facilities people are going for multi state chemistry.

Now let us say that this kind of thing is really not occurring in nature are you are you getting my point; that means, how this reaction will be taking place let us say you know imagine that there is a certain chamber in which hydrogen oxygen’s are there and you have raise certain temperature. Now there will be of course, even if you are not raising the temperature there will be also colliding each other right because of randomness of the motion and then it will move, but when if you increasing the temperature what will happen it will be basically colliding with the higher velocity or momentum. So, therefore, there will be some breaking of bond or forming of new bonds will be taking place.

And if that is happening; now what is the likely to be happen you know right is that we will taking some four reactions to illustrate how what will be happen? As I told this is known as also global reaction right and this global reactions wont occur in nature it is only for our own convenience we have devise it ok, but now what will happen if hydrogen oxygen is colliding with each other right imagine, then what will happen it will go to H O 2 plus H.

In this case what is happening O 2 is being broken right; that means, O 2 is there 1 bond is broken here 1 bond right in the left hand side right this is hydrogen is being broken right hydrogen is being broken and then it is joined with O 2 and became hydro.

Peroxide right hydro peroxide H O 2 is known as hydro peroxide right yes or no hydro peroxide right and plus H; that means, one bond is formed which is likely to occur you may say that why not H 2 plus O 2 can go to O H plus O H is it likely to occur as compare to this reaction I can also have a reaction H 2 plus O 2 going to O H and O H right is not it is it balance O H and O H is possible, but if you compare this reaction I if can say one a reaction right for just to segregate both the thing right that this is less slightly to be formed, why? Because it is in the reactant side three bonds are to be broken and here two bonds are to be formed.

So, therefore, it is less likely to occur as compare to reaction one, but both are elementary are you getting both are elementary. Is that clear? Now if it is there H and if you look at H what we call like H O these are radicals and what is the meaning of radicals? Radicals will be having unpaired electrons; that means, they radiate to make a bond right ok. See for example, if you are having ego right you cannot have a friendship with other or relationship with other right. That means you are having ego I am great.

So, similarly if there is a empty you know or electrons or mobiles are there will be exchange then taking. So, therefore, this H and O are very reactive and those are known as radicals and this can be very important for making the reaction to happen right in chemical reaction these are the things are very important.

And then this H radical will be colliding with O 2, because you know the O 2 is a double bond right. So, it is not that easily to break keep in mind that in the first reaction why not O 2 will break O 2 will be a stronger bond right double bond. So, therefore, H is likely two break; are you getting my point here, but H atom will be is radical. So, therefore, it will be you know more energy that it can break there is become O H and O.

In this case what is happening that again the single bond is broken and then one bond is formed right? So, and O H will be reacting with hydrogen that is also possible right and then H 2 O will form and H and H plus O 2 this is the forth reaction what I am trying to discuss H plus O 2.

Reacting with the M, M is a basically third body right this is M is third body. I have talked about that let me again repeat this, when this third body this is a tri molecular reactions right H plus O 2 plus M going to the H O 2 plus M right and this will be a inner body like nitrogen or may be some other molecules which is not participating in this reaction particularly that is known as a third bodies right.

And this if you look at this a very simple mechanism I want to illustrate and say that this is basically multi step reaction mechanism this is known as multi step reaction mechanism do not think that I can use you know this as the substitute for the global reaction; that means, hydrogen oxygen reacting in this code its not that now a days they are using you know something minimum 20 reactions right to stimulate the multistep chemistry for hydrogen oxygen and this one, but in earlier days people are happy with two step people are happy with four steps right, but today because of computational power we could manage to you know use more number of steps.

Therefore, the multistep reaction mechanism and whatever you do even if you do the 20 steps reaction mechanism, but sill whether it is making the nature or not that is a 1 million dollar question are you getting? Are you getting? And in methane I had taken in 25 years back the something around 40 reaction steps for my previous theories, but today people are taking may be 150 year 200 steps right and if you go for higher hydro carbons people are talking about 1000 multi step chemistry you know kind of reactions or people are talking about 1200 1500 like that.

So, coming back to that let us consider the arbitrary molecular reactions a b and we can find out reaction rate d C A by d t is equal to k C A A is your co efficient stoichiometric co efficient and C B this is also be stoichiometric co efficient. So, right this we have seen, but now keep in mind that this k is the specific reaction rate or rate co efficient whose unit is meter cube for kilo moles second and.

So, k depends on temperature and activation energy right are not discuss about that, but we will do little later on not on the concentration, because this thing is valid for the elementary reactions as for the law of mass actions and for finding out for this k right. We will have to invoke the collision theory and for that; what we will do? We will be looking at kinetic theory of gases right and which will be discussing in the next lecture, then I will have to go back to the collision theory and find out the expression for this specific reaction rate or the reaction rate co efficient right.

Thank you very much.