Fundamentals Of Combustion (Part 1)

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Lecture - 27
Elementary chain reactions

Let us start this lecture with a third process.

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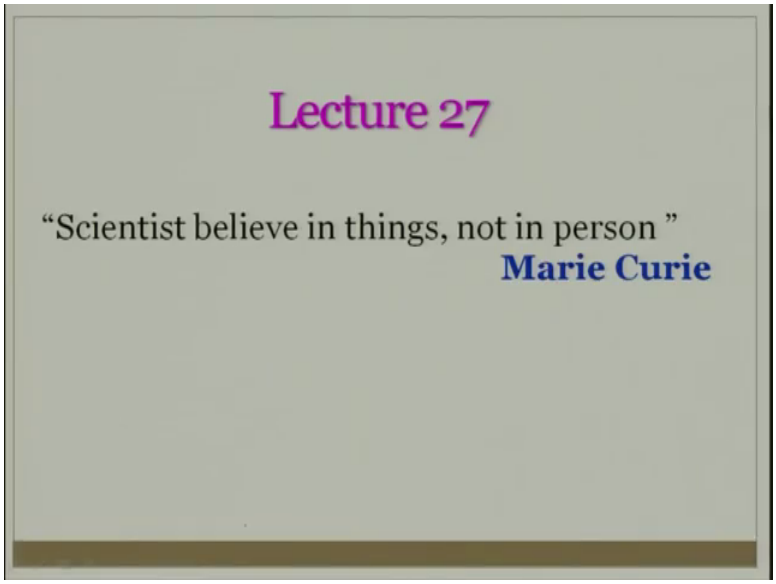

"Scientist believes in things, not in person" this is madam Marie Curie. You might be knowing she is a very you know great scientist. And let us recall what we learnt in the last lecture, we basically looked at series reactions parallel reactions and reverse reaction, how to handle basically and what are the it is ramification; because it is very important to handle the multi step chemistry particular the elementary reactions right. And today we will be talking about basically the chain reactions, because it is you know which is very important chemical reaction; you know not only takes place in series and parallel it will be in the chain right.

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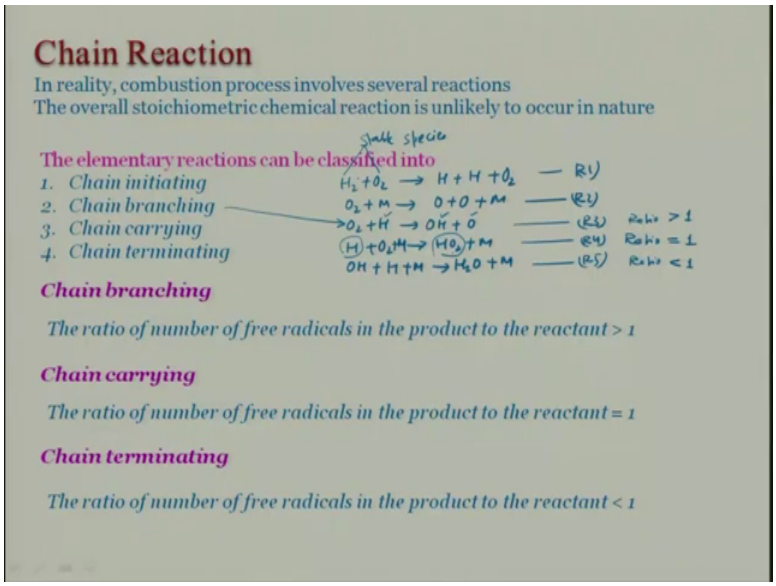

And chain reaction is very important and you might be; knowing that you know chain reaction also not only occurs in chemical reaction, it also occurs in nuclei right reactions. So, and it also occurs in our day today life right, we can say oh there is a chain reaction; that means, suddenly something is happening right. So, will have to be you know a wait about that in reality combustion process involves several reactions and the; whatever we see that stoichiometric chemical reactions, whatever we consider we always happy with the stoichiometry right, but that need not to occur in nature as such, because there is a lot of things which will be going on.

So, the if you look at will be now, classifying these reactions into four categories, which those are basically chain initiating reactions, chain branching reaction, chain carrying reaction and chain terminating right. So, we will have to see who initiates you know the things, because the initiator is very very important you know like in our spiritual (Refer Time: 02:31) the guru is known as the initiator right.

And even in teaching also that is, they are basically initiator is a you student has to learn you know ok. So, the therefore, initiation is very important and similarly branching it will be branch into something and it will be carrying forward the meaning is very obvious like means, you will be taking carrying forwards and it will be also terminating right. Now question arises how you will you know define these things, how I will identify; whether it is a chain initiating or chain branching or chain reacting. For

example, if I consider right this is let say if I say this is H 2 plus O 2 is going to H plus H plus O 2 right are you getting.

Now, what kind of reaction it is? Let me write down another reaction O 2 M is getting into O plus O plus M you know M is basically third body reactions and I can write down another reaction O 2 plus H is getting into O H plus O right. Now, in this reaction which is chain initiating which is chain terminating, which is chain carrying or which is chain branching right? Please think about from this let say let me write down further right H plus O 2 plus M H O 2 plus M O H plus H plus M getting into H 2 O plus M. Now, if you look at if I say this is you know reaction 1 this is 2, 3 4 this is 5 right. I am writing for basically say, that is the reaction right. Now, if you look at the first reaction what you call.

Student: Initiating reaction.

It is initiating why; because the stable species are there in the reactant these are stable species these two are stable species and, then the radicals are being formed right, but if you look at this O 2 and M O plus O is the same thing O 2 is the stable species. Of course, M you do not know M is the third body you know like it is not participating, but it is it is presence is required right you cannot call it as a catalyst reaction ok, but; however, this presence is required you know like, let say there is a old man in the house, but his presence he would not do anything, but his presence is required, because he will give inspiration to for you people to do work you know right, like your grandfather or grand grandfather right he would not be doing anything.

So, similarly third body is like that ok. So, this is again chain initiating, but the reaction three or the third reaction O 2 plus H going to O H plus O, what is this reaction is a branching or carrying?

Student: Branching.

It will be branching how I will decide how I will decide if the ratio of number of free radicals in the product to the reactant that of the reactant then greater than one it is chain branching right for example, in this case in the reaction three these are two right and in this side radical is one. So, therefore, it is ratio of radicals right between the product and the reactant right I can say the ratio is greater than one. So, therefore, it is a chain

branching reaction therefore, this is a chain branching reaction right and similarly you can say chain carrying reaction when this ratio is equal to one this is equal to one; that means, if you look at this reaction 4 this is a radical right H O 2 and this side the radical is h; that means, one right reactant the product side radical one and reactant side radical one therefore, ratio is one.

So, this ratio I can say ratio is equal to one and in chain termination, what it would be stable species will be that is one, but if you consider from the radical point of view it will be always less than one right the it will be ratio is less than one therefore, that is known as basically terminating and chain initiation is will be other way around right, the always the reactant side will be stable species and product there will be some radicals right it will be greater you know than one or.

So, it is similar to chain branching, but keep in mind that in the reactant side always stable species will be there right will be 0 radical will be 0, in the stable species in chain branching radical will be there in the reactant as well in the product; that means, it will be there in the reactant and product ok.

Now that is very clear you can identify, which is chain branching chain initiating, chain carrying and chain terminating reactions by this process or the procedure.

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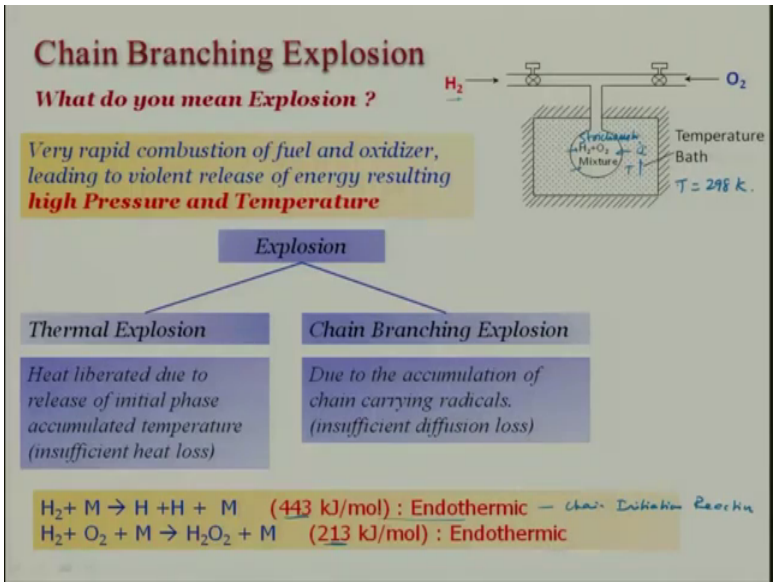

Now, let us look at you know this chain branching and if it is more radicals are formed in the product, than the reactant then it may lead to explosion, but what do you mean by explosion any idea any idea; what is the meaning of the meaning of explosion you might have heard like.

Student: (Refer Time: 10:05).

No.

Student: (Refer Time: 10:07).

Uncontrolled combustion you are saying for example, if I say there is a pressure cooker which is busted out right, there is no reaction taking place yes or no is it reaction taking place pressure cooker I will heat give lot of heat. And then it will be bust out or I will take a balloon you know and give lot of this thing there is no chemical reaction taking place ok, but it will bust out; that means, there will be sudden pressure.

Student: Release of energy.

Release of energy which will we can define that way, that is the little better one right; here what we are doing right; this basically we are saying look chemical reaction is taking place right, but in nuclear reaction nuclear explosion right, because there will be nuclear reaction will be going on, but basic is idea is that there will be burst of energy which will be causing some kind of a you know pressure change sudden and temperatures and other thing.

So, therefore, we can say that in our case it is the very rapid combustion of fuel and oxidizer that takes place leading to a violent release of energy, that is very important violent energy of release right, resulting high pressure and temperature change right this will be of course, this this is caused due to the high pressure and temperature in a very closed container right.

So, therefore, explosion can be divided in two categories one is thermal explosion right, other is chain branching explosion or you can say chemical explosion you know you can say in our case of course, there will be nuclear explosion right. So, thermal explosion means basically heat liberated due to initial phase of accumulated temperature or you are supplying the heat right.

Heat is being supplied and the loss is minimized or loss is not there or loss is less as compared to the heat input to the a container close container particularly explosion would not occur if it is open you know are you getting unless pressure builds up and other things it would not bust it out right. So, that is basically occurring this thermal explosion occurring due to insufficient heat loss; that means, more energy is being pumped into right.

The balance if you look at more energy in getting in chain branching a chain branching explosion. In this case what will be happening this is due to basically accumulation of chain carrying radicals. For example, in chemical reaction H O H you know these are all very you know what you call problematic radicals I cannot say problematic radicals problem at radical from the explosion point of view for the chemical reaction without that you cannot have a chemical reaction right.

So, those are good, but if it is misuse you know, then that will be creating a problem of explosion and this is being accumulated; that means, whatever being generated is not being consumed right; it is like your the rich people became going astray you know they are accumulating.

So, much of money right or so, much of power being accumulated it will cause the explosion. So, therefore, that is a anything you know accumulation is a bad thing that is why our you know scripture says you always donate keep the balance right. So, now, let us consider a case in which let say stoichiometric hydrogen oxygen mixture is there right; and I am keeping this is like a bomb you can say is a closed vessel and supplying the hydrogen and oxygen.

After that I am closing it right these are all closed right; that means, it is a closed right it is a closed bump kind of volume control you know volume is remaining constant I can close this ok. And then I am increasing this temperature, temperature bath means where I can control the temperature right. So, that temperature bath I can goes on increasing. Let us say this t t of the temperature, but then there will be heat transfer right and it will be getting into from here to that this heat will be getting into right.

Now, what will happen there will be at if it is at ambient temperature if t is equal to 298 Kelvin start with what will be happening; there will be no reactions you know like all the forward reaction will be same as the backward reaction almost it will be nothing will be

happening, but if I go on increasing the temperature further, then some chemical reaction will start and it will be basically stable, then it will be metastable kind of condition earlier you know it becomes unstable right. And then reaction will be taking place, if reaction takes place heat being released right if it is heat released what will happen is a constant volume.

Student: Pressure.

Pressure will go up and again there will be some accumulation of thing will be occurring. Let us look at what is happening; if I say that hydrogen you know will be reacting with a third body right and getting into this H and H radicals. This is basically what kind of reaction this is. First one what is the reaction here chain initiation right reaction. Now this is endothermic in nature see unless you give heat it will not occur ok. Are you getting, but there is another reaction this is again hydrogen oxygen is the react with third body it will go into H 2 O 2 write M; and again this is the endothermic keep in mind that this is if you look at this is the higher right.

As compared to this reaction, because these two can go parallel you know like hydrogen can be composure hydrogen get into H 2 O 2 and one is and this will be the first reaction if you look at this one right will be occurring at a much higher temperature as compared to second one is not it, because the energy requirement for you know the two, that it will be heat has to be supplied for this for this reaction take place right.

So, now if it is occurring there will be certain temperature, if you look at you will go to the self ignition temperature if you go on increasing right, because I am not igniting here. Then the reaction will start which will be vigorous right the pressure will increase, if I pressure will increase what will happen explosion will occur or not right.

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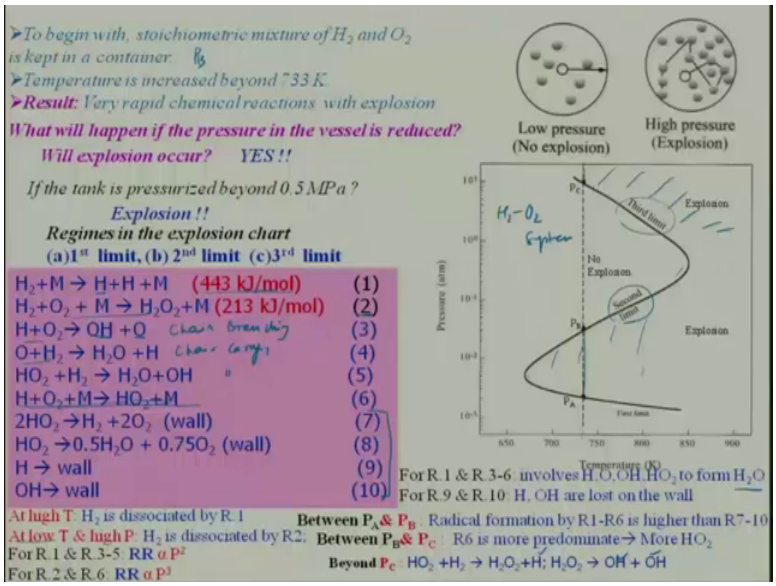

Let say as I told to begin with the stoichiometric mixture is taken is kept a container stoichiometric mixture at a certain pressure right; and you will go on increasing temperature in that container by the what you call your like thermal bath right, by that I can control the temperature and let say it is increased beyond 733 Kelvin, where the reaction will start and then you know it may lead to explosion right. So, the rapid chemical reactions will be take place leading to the explosion. Let say at certain pressure right at certain pressure let say PB right at pressure PB it is occurring.

Now, I will reduce the pressure right what will happen will it like explosion will occur or not right. Actually explosion will occur even if you are reducing right, but generally notion is that the pressure is that will release no, because this is a chemical reaction you do not know what is happening; and if tank pressure is pressurized beyond certain values right. Then you know again explosion may occur right.

Now in between some range explosion would be occurring even though temperature is high higher than the; it is self ignition temperature and the pressure is moderate right. So, if you look at that if you conduct this experiment and you will find a curve like this right. If you look at suppose I am here right at PB and PB; that means PA to PB this explosion is occurring this is this is the range where explosion will be occurring.

But, now I shall increase the pressure right what will happen; there will be no explosion even though I am increasing, but if I reduce the pressure explosion will be occurring

right and there is no explosion, but if I go beyond in this region, but if I will go beyond this right, then explore for the same temperature I am talking about at the same temperature keep in mind, because there are two variable I cannot change just to explain this thing I am saying I am keeping I am conducting experiment as that temperature will be remaining same only pressure will be changing.

So, pressure beyond that there will be explosion, because this region also explosion is occurring right. Now, it is quite interesting this curve is basically s shape you can say inverted s shape right s we write in other way inverted s shape curve and this is valid for what is that hydrogen oxygen system right or you can say n 2 system or I can say this is hydrogen oxygen system right. And similar curves you can get for co and s O and other things I will not be discussing.

But you can look at maybe (Refer Time: 21:15) book or some other combustion book you may find right not in my book. Now question arise is, why it is happening; we will have to look at it qualitatively looking at the some reactions right. And there are regimes three regimes are there this is the first limit right regime and this is your second limit right this is your second limit and this is your third limit beyond, which you know explosion will be occurring.

And let us consider these reactions see you can take more reactions as well, because it not that all this and only this much reaction will be occurring there will be several reactions I have shown right. I have taken only just to explain certain point's right. Let us look at what is happening; in this reaction I have already explained that in the reaction one right at high temperature it will be occurring, because this is endothermic in nature right and as compared to the reaction 2, these are all chain initiating reactions right, but at low temperature and high pressure H 2 is dissociated by R 2 this reaction 2 right, and for reaction 1 and reaction 3 to 5 except reaction 2; the if you look at reaction rate is proportional to P square, why; because bi molecular reactions right these are bi molecular reactions right, yes or no?

So, therefore, the second order reaction is there therefore, it is required to this one, but whereas, the reaction 2 this is the reaction right this reaction and reaction six these reactions right for that this is reaction rate is proportional to power to the pressure of three pressure cube; that means, you know it will be more the reaction 2 and reaction 6

will be more pressure dependent as compared to the reaction 1 and 3 to 5 these are all if you look at chain branching, if you look at reaction 3 is chain branching reaction 4 what you call the reaction 4 is; what this is chain carrying this is your chain carrying is not it and this is your chain branching and this is again, what you call chain carrying right.

This is also chain carrying and these reaction if you look at the reaction 7 to 10, these are all terminating right, because a you know 2 H O 2 going to H 2 and this table space is not oxygen it is getting into wall and then converting and similarly here and H of course, can you know bumped into wall and reduce energy is well way O H also.

So, and keep in mind that for reaction one and reaction 3 to 6 involves; what is that H, because these are all radical H O right O H right O H and H O 2 these are all you know radicals, which are required to convert the hydrogen into water right and of course, 9 and 10 I have already told these are basically O H and O H are lost getting into or colliding with the wall of the container right, because this will be having lot of energy level at elimination.

So, if you look at if the low pressure, what is happening; if H O 2 is being formed right by the reaction R 6; this reaction right H O is formed and if it is happening at low pressure this is a very you know what you call in you cannot say inner, but it is an un not much reactive as compared to H and O H, H O 2 although it is a radical, what will happen it will go and heat to the wall and lose it is energy, then as a result you know it will not lead to the explosion, but where as a high pressure, what will happen; it will be getting and bumping into others and then some radicals are formed.

So, that it will be leading to explosion. So, therefore, at between PA and PB radical formation by R 1 to R 6 right ok, are much higher the more radicals are formed as compared to the reaction R 7 and R 10, R 7 and 10 is; what this is radical being terminated right. These are terminated remain consumed right, without much you know branching occurring. So, therefore, these P right radical formations are highers.

So, therefore, there will be explosion in this region right PA and PB, but in P B and c r 6 is more predominant right this 1 and more H O 2 will be formed and, which are not that reactive, and if the pressure is moderate you know like in between it is not very high right you can consider this to be relatively low, then there will be no explosion right provided in this region between PB and PC no explosion right.

So, and if you go beyond PB PC values beyond this pressure this is the higher values, then what will happen H O 2 and H 2 is going to this H 2 O 2 and this will be right and H is radical is born formed and H 2 O 2 is going to O H O H. So, more radicals are being formed and that will be because H O 2 which was not acting in this region between PC and PB, but when pressure increases that became more active, because they are colliding with the hydrogen colliding and then giving to the more radicals and these radicals are formed the more pool, that means more explosion will be occurring are you getting this point.

So, therefore, we need to I mean like you know look at the importance of the reactions in certain pressure range which is more important and that will lead to the explosion and certain reactions are not important. Particularly, this is being explained you know in terms of chain branching reactions right, because if it is branched further then, what will happen; explosion if it is branch being stopped it is not going into then it will be what you call explosion would not occur.

So, if you look at even more these things you can avoid the explosions to occur also you can device something and that is being done routinely in our case. Suppose, there is a problem; so what will happen you clamp you know 144; suppose that is a some right, because they will be spreading you say you party were and, then control it similar way you can also control the explosion provided you know which radicals and which is the pres[sure]- what is the pressure range what will be you can you know how what the occurrence of the explosion.

So, with this I will stop over we will be discussing the next lecture about basically how to handle elementary reactions by some certain techniques will be developing to minimize the number of reactions and also how to handle right.

Thank you very much.