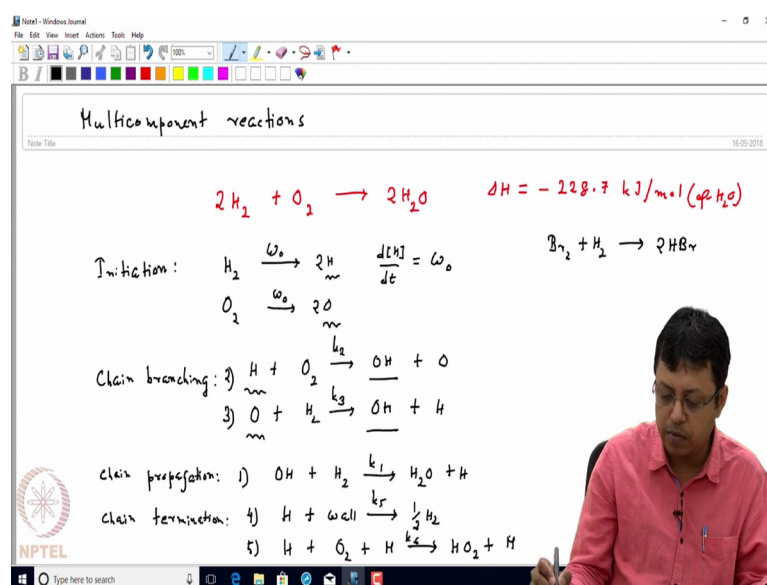


Advanced Chemical Thermodynamics and Kinetics
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Lecture - 20
Advanced Topic in Chemical Kinetics - 2

Hello everyone. So, today we will be discussing about applications of photochemistry, and the reactions will be considering are called a multi component reaction.

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So, it is known as multi component reactions. And under multi component reactions we will talk about two different kinds of reaction. The first one will be talking about combustion chemistry. And the second one will be particular example of a atmospheric chemistry. Now, for combustion chemistry we will be talking about the one particular very well-known combustion reaction; that is, a hydrogen and oxygen reaction to form water. Now this reaction is one of the very well-studied reaction and as you know the stoichiometry of the reaction is something like this $2\text{H}_2 + \text{O}_2$. Now this is the overall reaction and this reaction is exothermic in the sense that heat is produced in the reaction.

And if you remember from your thermodynamics I mean class, that for exothermic reaction the system releases heat. So, it is actually negative in that sense. So, the it is exothermic by 228.7 kilo joule per mole. This per mole is a per mole of water per mole

of the product. And but the mixture of these gaseous hydrogen and as you can see that it is a huge exothermic reaction.

But the problem is that the mixture of hydrogen and oxygen, there are very, very much kinetically inert. And the reason being they have a they need a huge activation barrier so, for the reaction to proceed. Now, this reaction can be initiated very easily by a spark or just amount of any kind of spark or a fire can actually initiate this reaction; which actually provides the necessary activation. And then what happens some radicals are initially generated and those radicals actually help to proceed this reaction further to produce water.

Now, there has been many proposed mechanism for this reaction. And one of the very well accepted mechanism which I am going to write here is basically involves several steps. And the first step if you remember that hydrogen, the radical reactions which we talked about earlier which was this bromine plus hydrogen to form, 2HBr that reaction we discussed. And that was a particular example of radical reaction, where we are talking about the radicals were the bromine radical and the H radical hydrogen radical.

Here and also we will be talking about similar radical chemistry. And there we talked about the initiation of the process; where actually first the radicals are generated. Here also we will be talking about an initiation process, but this initiation can be through the spark to photochemistry, through many other activation mechanisms. And then what we are saying is first the hydrogen as well as the oxygen they produce the radicals, which is H radical and O radicals. And the rates at which they produce we are just simply write it as ω_0 .

So, this ω_0 is just over all rate. So, in the sense, it is not actually rate constant. So, when we talk about say dH/dt . If I have a say that constant something like k . So, then we have to write it the equation as $2 \text{ into } H_2$; this 2 is coming because actually there are 2 hydrogen atoms are produced. But in this case we will not use this convention. What we are saying that this overall rate is itself ω_0 . And this rate is same for hydrogen or oxygen, because it is basically the supply of the energy. So, that is the rate of supply of energy that is dissociating these bonds. And then we have actually chain branching. Now, what do you mean by branching, I will come to that.

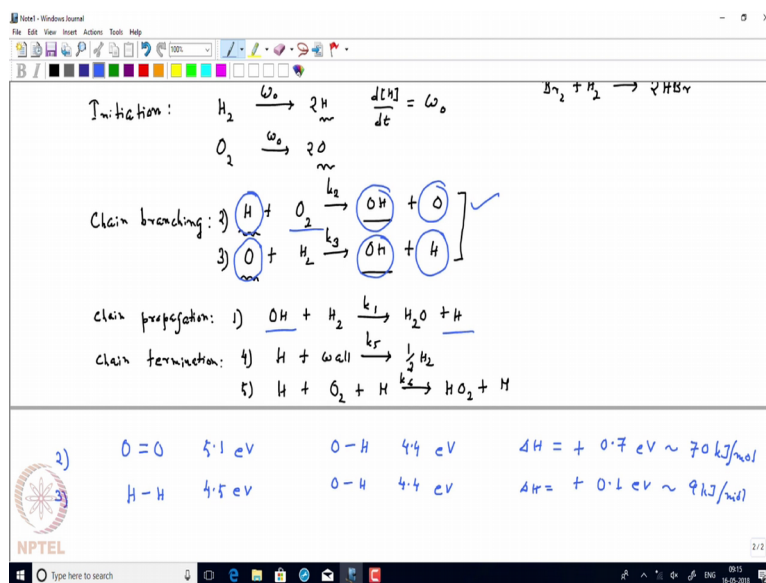
So, we have $\text{H} + \text{O}_2$, and then we have $\text{OH} + \text{O}$. Now this reaction we name it as number 2. And then this is basically the rate constant according to the number of the reaction I am writing at k_2 . And similarly there is another branch reaction which is $\text{O} + \text{H}_2$. Well, basically the radicals as you can see formed are actually reacting with the hydrogen and oxygen. And I can call it as a k_3 and we have $\text{OH} + \text{H}$.

And then also we have the chain propagation, which we are naming as number 1. So, this numbering is according to like one of the proposed model, but this is just arbitrary numbering. So, you may wonder why I am writing 2 and 3 first, and then one letter the reason is usually you write the chain propagation step first and then the branching. But for the propagation step you need the H radical which is a product of the branching reaction.

So, this H radical now reacts with the hydrogen to produce that I that is why I am writing at k_1 . And again this is a very arbitrary the k_1 notation. Water plus H and of course, you have some termination. So, chain termination, and we have 2 reactions. One is basically the H radical, it can just react instances collide with the wall to form half H_2 . And similarly the H radical can be abstracted by oxygen. And third body this third body can be the wall or something else because when H and O_2 reacts you have an exothermic reaction. And for that some heat is released.

So, there should be some something to absorb that heat otherwise the bond will not form. Now, the interesting thing what you notice here is that we have written at the 5 steps.

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Now, if you look carefully at these branching steps. So, there are initiation steps, and then this branching step if you, look now why do we call it as a branching you see that we actually started with one radical here with means some other color. So, we have actually used only 1 radical here H.

But then we are getting actually 2 radicals OH and O. So, basically one radical is producing 2 radicals or the radicals are branched out. Similarly, the oxygen there is one radical and it is now producing 2 radicals OH and H. So, here also it is a branching example. Whereas, the propagation is something like you start with one radical and that generates another radical. And that radical of course, will again the H radical will of course, as we can see in step 2.

The H radical will also generate back to the OH and that is how it basically propagates. And then there are termination reactions, but as we have you can see we have not written any termination reaction for oxygen radical because, there are some issues because you have. So, also considered the exothermicity and endothermicity of these reactions; so, let me give you some values of this reaction you know which is endothermic and exothermic. Like, for example, we have some values here. So, suppose the oxygen oxygen so if you think the branching step number 2. What you see here the O O bond energy so, that is broken, because you can see here oxygen oxygen bond have to break.

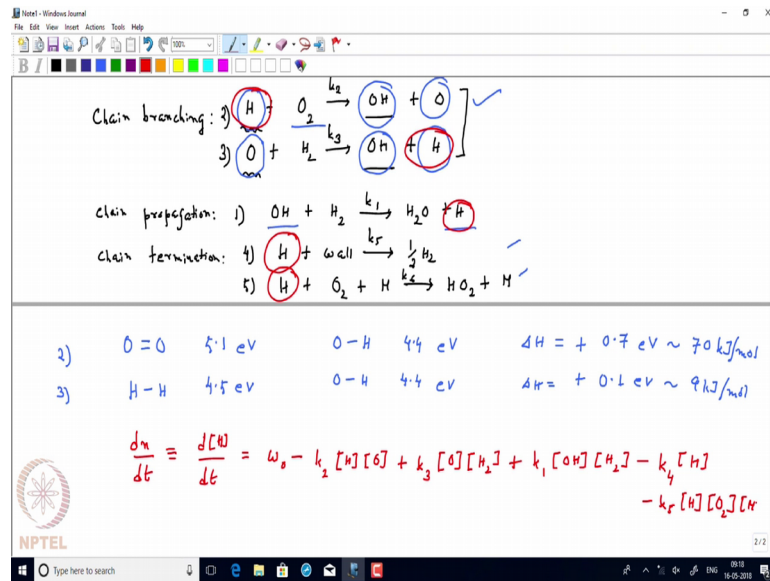
And that bond energy if you take about say 5.1 electron volt. And then you are forming and OH bond energy.

So, let us just take that value OH bond energy approximately is a 4.4 electron volt. So, the this step 2, it is actually what you are getting is. So, you are basically you had a oxygen oxygen bond which is much more energetic. And then you are actually forming a bond which is less energetic. So, basically you have to supply energy. So, this reaction is endothermic. So, delta H is plus about it will be if I take the difference, it will be about 0.74, 4.4 and 0.7 is 8.1. And which is approximately about you can always convert it to kilo joule per mole. It is about 70 kilo joule per mole endothermic whereas, if I consider about step 3, where actually I broke up H H bond. And H H bond energy is 4.5 electron volt. And the OH which you are forming is 4.4 electron volt.

So, 4.5 and 4.4 and this will be about plus 0.1 electron volt the delta H. Since both cases you can see step number 2 and 3 OH radical is; so, which is approximately equal to 9 kilo joule per mole endothermic. So, thus we see that these reactions this 70 kilo joule per mole at room temperature it is less probabilistic because is much lower than kbt, a higher than kbt. And then for this reaction is on the order of kbt and you can actually have it more feasible. So, step number 3 will be more feasible. But step 2, we are actually we are making the O 2 bond, that rate will be much slower. Now there are all these details which you can actually approximate and you I mean which you can use to make some approximations.

Now, let us first try to understand: what is basically the rate of the reaction or later say the change in concentration of the H atom. So, c or the rate of change of say free radical density. Now the amount of free radical which will be present in this like in this mixture is mostly the H radical. And because H radical actually is the controller of this reaction as you can see that we have written the termination also for H radicals, but not for O radicals.

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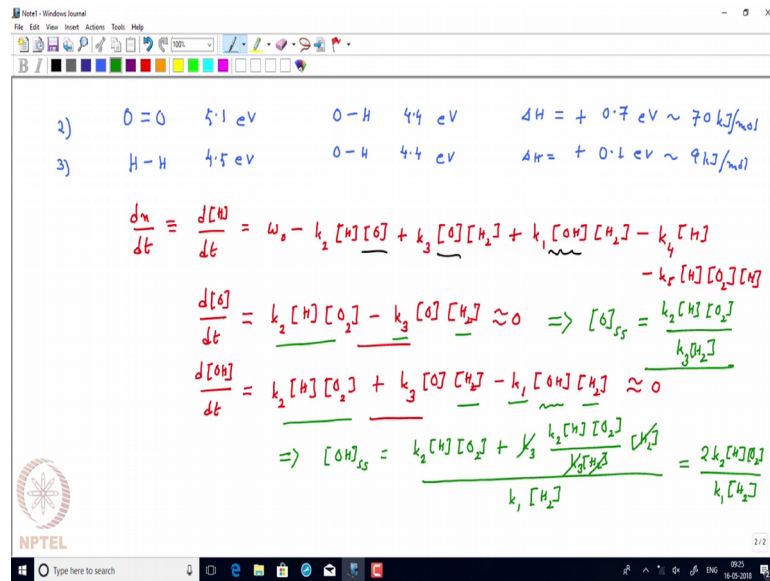


And since H radical is the controller of this reaction, we are writing this let me use some other color. So, we can write this equation as the radical concentration change in radical concentration, which is equivalent to saying the rate of change of dH dt of hydrogen atom concentration of hydrogen radical concentration. Now first step was the initiation so, that will be as I said, for that step dH dt was just omega 0. So, just write omega 0, and then we have actually the branching steps where this is being consumed.

So, it will be k 2 into H into O, just follow the kinetic equation a stoichiometric equation where I mean these are all elementary steps remember. So, that is why just by looking at the equation I can write the rate equation. And then similarly in the third step H atom is formed. So, we have taken into account of this step, now we are taking into account of this. And then H is formed so it will be a plus sign will have k 3 times O times H 2. And then what we will have is the 4th step were actually again we are having the H atom forming.

So, it will be plus sign k 1 OH into H 2. And then we are again the termination step means the H will be vanishing or H is basically being destroyed or consumed in the 2 termination reaction. So, it will have minus sign. So, it will have minus k 5 into it will be first k 4. Because that is the 4th step that k 4 into H and then again another termination reaction which is k 5 H into O 2 into M. Now, what are the other 2 radical species?

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Those are oxygen radical species; and as I said, the oxygen radical concentration will be much less throughout. So, which means that we can actually approximate after considering the energetics which we already discussed right the O O bond cleavage is, and forming the wage come simultaneously that reaction rate will be slower because it is highly endothermic. And that will be like wherever you get the oxygen atom forming.

So, as you can see that this process, as I am saying this is a bond energies are pretty high. And what I am also saying that this I can actually ignore the first step also, saying that reaction is mostly controlled by H radical formation. So, I can actually ignore this step. And then because the rate will be much slower, the reason is actually or as you can see the H radicals are being in the propagation step, actually the H radical is the thing that is being formed.

So, what we see here is that we can actually ignore the formation of a O radical. That step that we will not ignore we will not consider any omega 0 for this d or dt step. And again this is an approximation, after considering the energetics. And then I will have minus k 3 O into H 2. So, I am considering only these 2 steps; where actually oxygen atom is formed an oxygen atom is consumed.

And similarly, I have one more radical which is the OH radical which, is being formed during the course of the reaction as you can see here. So, I will have for OH radical. The kinetics will be d OH dt. That will be k 2 H O 2 plus will have k 3 OH 2. Because these

are the 2 steps these 2 steps, where basically in both steps. So, H radical form, but in the first step O radical is from second step O radical is consumed. That is why in O radical equation I have a minus sign. But here actually have a plus sign because it is for OH radical. Plus, as you can see there is also OH radical in the chain propagation step which is being consumed. So, I have to use minus $k_1 \text{ OH}$, then have a look at the equation minus $k_1 \text{ into OH into H}_2$.

Now, what we are saying is as follows. So, we have actually written the kinetic equations, rate equations for 3 radicals. One is H, one is oxygen and one is OH radical. Now the H is the main, I mean, main components here. And you have multi radical components here. But what we are saying that this H actually when the reaction proceeds, this H radical keeps on increasing, and what will happen is that this H radical concentration is not actually small.

Rather OH radical and O radical concentrations are small. And it is kept a small throughout the reaction. So, we can actually make steady state approximation for these 2 radicals. OH radicals and O radicals, but not for H radical. Because H radical is a one that you want to solve, using the values of O radical and OH radicals. Because as you can see we need to those follows O radical is here, O radical is here, OH radical is here and here also yeah. So, these things we have to replace.

Now, if you do that if you solve that these equations. So, what you will get is that this is very straightforward. So, I will get from here the oxygen radical concentration under steady state approximation. That will be it is pretty simple algebra, and you will find $k_2 \text{ into H into O}_2 \text{ divided by so this term and divided by } k_3 \text{ into H}_2 \text{ } k_3 \text{ into H}_2$. And similarly for from this equation, if I want to calculate the OH radical concentration which is here.

So, then what I will have is from this equation. The OH radical concentration under steady state is nothing but this term which is $k_2 \text{ into H into O}_2$, plus $k_3 \text{ into O and H}_2$, now for O I can use this I mean this expression; which is $k_2 \text{ H divided by } k_3 \text{ into H}_2$ let us just write it $k_2 \text{ H O}_2 \text{ divided by } k_3 \text{ H}_2$ and then I have a H₂ also here.

So, you have H₂ and then I will have divided by so, there will be a minus sign here. So, this is 0. So and there will be no minus sign. So, I will have $k_1 \text{ into H}_2 \text{ } k_1 \text{ into H}_2$. So, what do you see here this $k_3 \text{ H t H}_2$ gets cancelled out. So, what will be left with after

we do some simplification, you can easily see that $k_2 [H]$ and O_2 . This will be twice of $k_2 [H] O_2$. So, this is twice of $k_2 [H] O_2$ divided by $k_1 [H_2]$, if you get some compact form for these 2.

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The image shows a handwritten derivation on a whiteboard. The top part shows the differential equation for the radical concentration $\frac{dn}{dt}$ and its simplification to a first-order linear ODE. The bottom part shows the integration of this ODE to find the concentration n as a function of time t .

$$\frac{dn}{dt} = \omega_0 - \frac{k_2 [H] [O_2]}{k_3 [H_2]} + k_2 [H] [O_2] + 2k_1 [H] [O_2] -$$

$$= \omega_0 + \left\{ 2k_1 [O_2] - (k_1 + k_f [O_2] [H]) \right\} n$$

$$= \omega_0 + (f - g) n$$

$$\frac{dn}{dt} = a + bn \quad n = n, \quad a = \omega_0, \quad b = f - g$$

$$\int \frac{dn}{a+bn} = \int dt \Rightarrow \frac{1}{b} \ln(a+bn) \Big|_0^n = t$$

$$\Rightarrow \ln \frac{a+bn}{a} = bt \Rightarrow 1 + \frac{b}{a} n = e^{bt}$$

$$\Rightarrow n = \frac{a}{b} (-1 + e^{bt})$$

$$n = \frac{\omega_0}{g-f} \left\{ 1 - e^{-(g-f)t} \right\} \quad g > f$$

Now, we are going to use these values, to get steady state concentration of this not steady state concentration, what is basically the rate of the radical concentration which is identical to hydrogen radical concentration. And that we can do basically we have to write ω_0 minus. So, let us follow this thing it is $k_1 [H] O_2$ it is not $k_1 k_2 [H] O_2$. And O is here as we have seen here the O steady state condition. That will be nothing but $k_2 [H] O_2$ divided by we will have $k_3 [H_2]$, and then the second term is this $k_3 [OH]_2$.

So, there was a plus sign plus $k_3 [O]$. And instead of O will again use the expression for O . And we know that this $k_3 [H_2]$ as you can see will basically cancel with this $k_3 [H_2]$. So, ultimately we will be left with only the numerator terms. So, we can directly write it. So, it will be $k_2 [H] O_2$, and then you will have minus it will be plus $k_1 [H] [OH]_2$ this term.

And again as you can see that which radical has $q_1 [H_2]$ so, those w will cancel. So, ultimately you will have plus twice $k_2 [H] O_2$ and then so, in this case actually in this way. You can actually write all these terms. And you will see that these terms will

basically most of the terms, you can actually add and subtract and there will be some cancellation of the terms.

So, ultimately what we will get that I am writing is basically ω_0 plus twice $k_2 O_2$ and then we will have minus k_4 minus k_5 . Let me actually write it like this; minus k_4 into k_5 in into O_2 . So, this will be k_5 into O_2 not k_5 into O_2 . And we will have times M , because there will be this third body reaction.

So, it will give you a handout where show you all the steps I am not just for the to save time I am not going through all these steps. But you can practice it and see whether this final expression is coming you can derive and because, it is pretty straightforward. And then we will have H_2 here. And so, H_2 instead of H_2 we are just writing, H concentration were just writing it as n . So, this is this term as you can see this twice $k_2 H O_2$ those terms actually. So, the instead of H I wrote as n here.

Now what we can write about these terms is something like this. So, we are almost done, but will show it in a slightly different way. So, I am writing it look at it carefully as ω_0 plus f minus g into n . Where f is this entire term and g is these enter terms; so, k_4 plus k_5 into O_2 into M . Now this is just a again this is just a notation.

Now, what will happen? So, if I want to solve the equation for n . So, what will how it will look like? So, as you can see that this n will be ω_0 . So, this is just a differential equation. So, you have to move the dt on the other side. And then you put some initial concentration, but we are saying that at time 0 the n was 0 that way you can solve it. And as you can see that the it will be a logarithmic integration. Because it is a you can see that dx/dt is a plus bx kind of thing.

So, dx/dt is a plus b into x . So, what will do is a plus bx is dt . And then you integrate that it will be $1/b \ln$, it will be $\ln a$ plus bx . So, that will be equal to t after integration. And so, the limits are t minus 0. And here also we took it to be so that if I take the limits when let us say it is t and then evaluated between 0 and some arbitrary time. And here also when x was we can think. X is basically the radical concentration here dn/n is x . So, it was 0 initially and then at the final time it was x . So, when I put this 0 it will be nothing but $\ln a$.

So, what will be having is basically $1/b$. So, you can simplify this thing. So, it will be $1/b \ln(a + bx) - \ln a$. And that $\ln M$ plus $\ln a$ minus $\ln n$ you can actually take it as a ratio. And then whatever you have in the left hand side you can actually move it on the right hand side, because what is b is basically $f - c$. That will be multiplied with the t , and then you will get finally, an expression something like ω_0 minus b divided by $g - f$ times $1 - e^{-bt}$.

Let me just do it for you or so, but from this what we will get. So, this b I am just multiplying on the right hand side. It will be bt , and suppose I am using M extra minus sign. So, what I will have here? Just to I introduce the minus sign here. So, I will have here $\ln(a + bx)$. And which means actually a divided by $a + bx$ is nothing but e^{-bt} . And that you can now easily solve you can easily see what is a and b .

So, that way actually you can write this equation. Now you have to be a little bit careful like. So, I use the minus sign or we could have actually skipped a minus sign. So, that you write it as $1/b$ of the b thing we can move it on the right hand side. So, let us solve this integration. So, let us now solve this equation or integrate this equation. And what we are doing here is we can actually think that this integration is nothing but dx/dt , is a $a + bx$ kind of integration. Where a is x is n first of all. Where x is n , and b is ω_0 , and a is ω_0 so, that is how we have written. And b is simply $f - g$.

Now, so, the integration is dx by $a + bx$ is dt and then you integrate, between the limits 0 and t and you can approximate the radical concentration at time 0 was 0 at some arbitrary time it is x . So, these are very straightforward integral. So, this integral is \ln it will be $1/b \ln(a + bx)$; that we have to evaluate between the limits 0 and t . And then the right hand side is pretty straight forward this t .

So, what we can write? So, $\ln(a + bx)$ at t is not not sorry, t it is it will be basically x here. So, that is $\ln(f + bx) - \ln a$. So, that you can write it as $\ln(a + bx)$ divided by a . And that one you can write it as bt . And then I can actually rearrange it like it is I can write it as $1 + b/a x$ is e^{-bt} . And then I can solve it easily for x . And what I will get is x is nothing but it will be if I take the minus sign. So, I will have $1 - e^{-bt}$. And I will have here a $a + bx$. So, I have written, and then I will have here a by b .

So, that way you can actually rearrange all these terms. And then what you will figure out is the solution here will be M is nothing but ω_0 divided by b . So, my b was f minus c . I am just writing here as g minus f . And if I do that, then actually I will introduce 1 minus sign and that minus sign gets cancelled with this minus sign. So, I will have plus 1 here and also I will have a minus sign here. And instead of b writing as f minus c I am writing it as g minus f . So, I will just write it as g minus f into t . So, that will be final form of this final solution of this differential equation.

So, then this will be true if actually g is greater than f . Now when g is greater than f we can actually figure this out. What is g ? G is this term k_4 plus k_5 plus into O_2 into m , and f is twice k_2 into O_2 . So, this means actually g has the termination step. If the termination if it is a actually terminating first, that rate is first, then actually g will be greater than m . But if it is the other way; so, I have say g is basically a more than or g is basically less than f .

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The image shows a handwritten derivation and two graphs. At the top, it shows the integration of $\frac{1}{a+bz}$ to get $\ln \frac{a+bz}{a} = bt \Rightarrow 1 + \frac{z}{a} = e^{bt} \Rightarrow z = \frac{a}{b}(-1 + e^{bt})$. Below this, two cases are presented:

- For $g > f$: $n = \frac{\omega_0}{g-f} \{1 - e^{-(g-f)t}\}$. This is labeled "termination dominates".
- For $g < f$: $n = \frac{\omega_0}{f-g} \{e^{+(f-g)t} - 1\}$. This is labeled "more branching".

Two graphs illustrate the behavior of n over time t :

- The first graph, labeled $g > f$, shows n increasing from 0 and asymptotically approaching a horizontal dashed line at $n = \frac{\omega_0}{g-f}$.
- The second graph, labeled $g < f$, shows n increasing exponentially from 0, labeled "Explosion".

The NPTEL logo is visible in the bottom left corner of the slide.

We can actually write it in the original form, like in the sense that not with introducing the minus sign so, in that case f minus is positive. And I will have a minus 1, but that I can write it later. So, I can write it e to the power f minus g , e to the power f minus g which is a positive quantity into t and minus 1. So, that is the usual way people would write the solution. So, I have basically 2 conditions. One this g is greater than f means actually again the termination dominates. And then here the g is actually less than f ,

means actually you have the other condition; which means actually you are the H atom concentration.

Because if you see here, what is g and f , your you have accurately to cote k_2 in O_2 . So, this is basically the read of these processes. So, to figure it out from here; so, this $2k_2$ plus O_2 , these are basically the branching processes correspond to. So, if that rate is more so, we can actually say that it is more branching. Because, this 3 body term is only coming from termination and this is coming from mostly from the branching.

So, we will have our basically competition between whether it is terminating or whether it is branching. Also which, is important to note here. It will also depend on the pressure of a pressure of the oxygen also. So, we will come to that later pressure overall pressure of the gas. So, there can be actually other equation equations which we had not considered. Because this is a very complex process this kind of (Refer Time: 36:32).

Now, let us just try to draw or plot, what behavior we are going to expect for say n versus t . So, let us say if I actually plot this thing, and I am also saying that have actually normalized it. Or we do not need to normalize like the final value will be ω_0 into g minus f if I am plotting the first curve, where actually g is much greater than f , g minus f . Suppose this is the limiting thing. And then what you have? It is $1 - e$ to the power of minus a positive number into t .

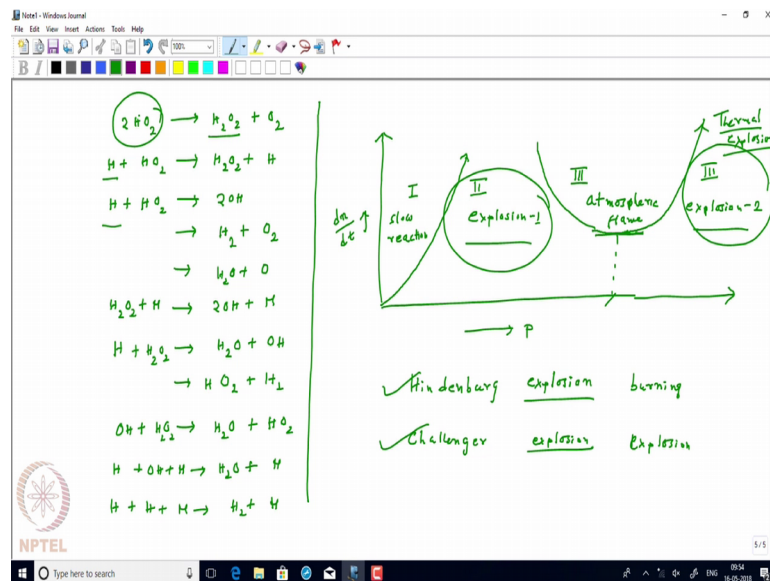
So, which means actually it will have growth. So, for long time, what we are seeing here is actually it is kind of saturating. Now when it is happening? Because actually you are having the reaction, but with a longer time or what you have is the chain is basically terminating. So, because the g term is more than the f term, and the g term actually includes the termination step.

On the other hand, if we have the other condition so, this will be the true for g is greater than m . If g is less than f , then you have actually what you can see here we have actually a plot which is ω_0 into f minus g that factor. But this part we will take actually emulate any other term because this is a positive part. And this is e to the power positive number into t . So, that then actually we will have a very, very high build up of the radical concentration which actually corresponds to explosion.

So, as you can see that if you do not have any control over the this radical branching or the propagation steps, which is basically dominated by H radical formation, and then actually it will be an uncontrolled reaction and then you will have an explosion. Otherwise if you can actually quench the reaction in the sense that you make sure that these radicals actually have a termination path, which is just because of collision or because of obstruction of this hydrogen radical by the oxygen molecule which is this reaction, this O₂H kind of species.

This species is by the way spectroscopically identified in oxy hydrogen flame. And that is why people proposed this particular pathway. And then actually you can have you can actually explain under what condition you will have the termination dominating. Under what condition actually you have actually radical thing I mean radical production or branching dominating in those cases this will be uncontrolled or explosion. Now, there will be also another other pathways which is much more difficult to analyze.

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In the sense that you can actually have this H O₂ species which is very, very interesting, which I said that this is spectroscopically has been identified in the oxy hydrogen flame. That also has its own interesting dynamics in the flame. And then it is very much a pressure dependent that I am going to discuss briefly. And then actually it these pieces itself interprets. And it actually can produce H₂O₂ and many other species.

And then this $H + H_2$ as you can see, I am just writing the equation one again because there are multiple species formation. We can have OH radicals also again generating from this H_2O_2 species. And then we can have $H_2 + O_2$, sometimes we can have $H_2O + O$ radical back. And then there are many other events like $H_2O_2 + M$. Again M is the third body, it is in this case it is a second body it can be something else anything else like it can be oxygen itself it can be the wall. It can be the hydrogen itself.

And you have a very, very interesting chain of reactions which all will participate if we have an enhanced amount of this H_2O_2 . Because these are all H_2O_2 initiated reaction because that is producing H total and then H_2 has its own interesting photochemistry. In this case it is not photochemistry it is basically the radical chemistry; which is initiated photochemically or by a spark. And we will have $O_2 + H_2$, $H + H_2O_2$ it will be $O_2 + H_2 + H$. This will be OH_2 or H_2O_2 that you can get. And then similarly you can have many other reactions like $H_2O + H_2O_2$. And you can have also the 3 body reactions like $H + H + OH + M$ which is $H_2O + M$.

And then again $H + H + M$ you can have $H_2 + M$. Now you can see there are the complexity of this entire hydrogen plus oxygen water reaction. There are enormous numbers of side reactions or the small elementary reactions that can happen, and in order to explain the overall thing. You have to study each of this reaction think about their thermodynamics, how much they are endothermic how much they are exothermic how much they are contributing, all these things will come into picture.

Now, what finally, we are going to conclude this section which is basically what happens in reality. So, if I suppose plot the rate which is the $\frac{dn}{dt}$ thing. After solving all this thing, you cannot of course, solve it analytically you have numerical solution. So, in a very early stage when you have actually the propagation is or the branching is controlling. So, you have zone where actually you have an explosion. So, this is a we call it as a zone 1. So, here actually the x axis, I am plotting as a function of say pressure.

So, if I increase the pressure so, I can have a I mean explosion and a very, very early pressure range. But then so, it is basically initially it will be a slow reaction, but eventually there will be a explosion. And here actually it is a slow reaction. Slow reaction in the sense so, this curve is actually combination of these 2 curves which we

have drawn. Like I had I will have a termination if termination dominates so, will have an kind of explosion. So, what I am saying is that overall I will have a growth something like that.

So, in that very slow reaction rate means actually have very low pressure, and then chances of getting heated the chances of getting the d being deactivated after colliding with a wall is basically much less. And then you have an explosion zone, and this is called explosion 1 zone. And then interestingly if you keep on increasing the pressure, sometimes what you will have here is that you will have a very interesting quenching reaction. Because now, the H atoms will be further extracted because as we can see these H atoms as you if you increase the pressure; you can actually generate this HO two kind of species and then this HO 2. Now can actually abstract this interesting species H O 2 can now extract the H atoms.

And then what you will see is that is you will see a drop in the reaction rate. And so, you have a region 3; where actually you will see things are burning it is called atmospheric flame. So, at a higher pressure you may see burning, but if you keep the pressure in a very high; so, what will happen? The enothermicity of the reaction will actually control the x will actually lead to explosion again. So, that is why you call it as a explosion 2 region; where due to the very high pressure. All these reactions are happening a lot of heat will produce that causes the explosion.

So, this explosion one is due to uncontrolled rate of the reaction. And this explosion 2 is basically the heat generated because of the reaction. And then initially in between you will have a drop in the reaction when you will see things are burning, but it is not actually exploding. Because you have some kind of like decreased the reaction that I made it actually in kind of flat it is also kind of a steady state I mean kind of situation. It is indeed a steady state, but it is not a same steady state as we discussed like it is not a very low concentration steady state.

Now, this thing has been was actually observed, and what happened is that in the 1937, we just put it in the note we will show you an interesting picture. Where it was shown that there were 2 accidents happen. In one case there was an pressure hydrogen filled shuttle, and it is name was a Hindenburg. And that Hindenburg actually exploded, but then the photographic images showed that actually it did not explode it actually did burn.

So, a Hindenburg explosion you can actually Google it, and then you will find that this was not exactly explosion. This was actually burning. So, why this burning happened? Because it was lying at some pressure zone like here, and at that elevated pressure you do not expect, but actually you burn. And then for another example was the explosion of the space shuttle challenger. Challenger explosion there also people showed the photographic image showed actually, this is a true explosion.

Because it showed that it is kind of exploding, but then the question was why it is exploding they had a very controlled reaction. So, that this explosion does not happen. Then they figured out that when they made this special space shuttle challenger. So, what happened is that there was a faulty O ring and this which actually is at a pressure gauge. And that faulty O ring actually leaked, and I mean it was it is faulty and that is why a lot of gas actually leaked through it through the window.

And then what happened? It caused actually a huge change in the pressure, and for that the it very hot it actually fell in the very high pressure region which actually caused the thermal explosion to happen. So, this is kind of a thermal explosion where you have lot of heat is being released and that is your explosion. It has nothing to do with the uncontrolled radical reaction, it is more like I mean like a heat generated suddenly.

So, with there are interesting examples real life examples of this hydrogen oxygen combustor reaction because, this is used as a rocket well. There are many other important combustion reaction. One of them is actually this combustion of methane. And other hydrocarbons like acetylene, which we actually are also used to like whenever you use say cooking gas. So, it mix with oxygen and then it burns.

So, what is the chemistry for that? So, these are also a radical chemistry, and these are all there are also branching and other things involved and it is extremely important that you have to control the pressure because if it is not controlled, then actually you might have an explosion there has been incidents of course, you know you are aware of that gas cylinder explosion.

So, you have to be very careful in controlling the pressure and other things. So, that is that combustion is kind of controlled and you have a very good flame which is a burning flame, but not an explosion. Because so, that you can cook your food. So, there are many practical examples, but again we are not go into the details. So, in this lecture to

summarize, we have given you a flavor that what is most important part of this thing is that that under two conditions like you can have the radicals.

If the termination happens it will be the reaction rate actually will be quenched eventually that will happen at the extremely low pressure. Because you can think that molecules are not colliding with each other, but there is a fairly good chance that it just hits at the wall of the container. But if it is a moderately a high pressure, then actually there are a lot of collision. And lot of radical production, which might lead to uncontrolled reaction which is explosion.

But then again if you have too much pressure, then you have an interesting chemistry for this H_2O_2 species, which can actually quench further the reaction. But even in a very high pressure limit, you can have a thermal explosion because everything is I mean overall the reactions are exothermic. And then you have an explosion for explosion happening which is the thermal explosion zone.

So, we will just stop our discussion on this radical the first part of the radical chemistry which is the combustion chemistry here. So, in the next lecture we will be we are talking about the atmospheric chemistry, but there also we will be talking about similar things. So, in this lecture we basically covered the first part of multi component reaction. And which is the combustion reaction, and again we just gave you one example of the combustion reaction, which is hydrogen and oxygen combustion reaction.

Thank you.