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PROFESSOR: So we're going to start directly today and look at chain reactions. And explosions. So chain reactions, how many people have heard of chain reactions? Lot of people have heard of chain reactions. Have seen chain reactions done, in kinetics. No. Alright, well, then I'll do chain reactions. Chain reactions. Chain reactions are reactions that feed on themselves. And there are three parts to a chain reaction. There's an initiation step, which is where your reactant makes an intermediate. And that's usually a slow step. There's a propagation step, where the intermediate reacts with your reactant, becomes a feedstock. And then there's some intermediate plus maybe a first product.

Then there's that second intermediate, can further react to re-form the initial intermediate. And that's the loop. That's the loop of the chain reaction. Plus maybe a second product. And then there's a termination step. Which is where when your intermediate, I1, becomes a stable product. Or I2 becomes a stable product. Basically, where the intermediates come out of the loop. So if you look at this loop here, you have your reactant that comes into the loop. And then go around the loop. You create I1, and maybe a product comes out. Maybe I1 gets terminated, but most likely it keeps going around the loop. Creating I2, which reacts with, the reactant at some point gets included in the circle. And I1 comes again, and I2, and I1 comes, and I2. And every time you form I1 or I2, you may form some of the product. So this is the initial feed. Then you go in circles. Eating up R, spitting out products. Keep going in circles. And at some point the termination's going to win, and the circle stops, and the chain has stopped.

And there are two kinds of chain reactions. There's a stable chain and an unstable chain, where you get your explosion. Stable chain, or also called stationary, chain reaction, is where the amount of these intermediates, I1 and I2, are constant in time. So you don't build up any intermediate. So I1 constant in time, which is why it's called stationary. Then you have the unstable, or non-stationary chain. Where in that case your intermediate increases in time.

So in the example I gave here, you destroy I1 in the first step, you create it in the second step. Comes back, you destroy it, you create it, you destroy it you create it. For every I1 that you start out with, you end up with an I1. There's no change in the concentration of I1. But if instead I put a two here, than my reactant creates an intermediate I1. I destroy it. Create a new I2, the I2 decomposes, creates two I1's. So after the first cycle, let's look at the concentration of P2 here, after the first cycle here I have one I1, and make one P2. But I make two I2's. So now I have two I1's coming in here. So I have twice this reaction. I make two I2's. These two I2's form two

products. And now four I1's, two times two. These four I1's go through the process. I get four P2's. So third cycle, I get four P2's. And I get two times four, eight I1's. These eight I1's go through, and I get eight here. For cycle, et cetera. So I end up with something that goes like, so this is two to the zero power. This is two to the first, two to the second, two to the third, et cetera. Eventually you get two to the 25 or whatever after so many cycles. And if these are gas phase products, so if there's an exothermic process where heat gets created at any of these steps here, then you end up with a problem. The thing goes out of control.

Sometimes that's a good thing. If that's what you want to do. And sometimes it's a bad thing. Depends on what you want to do.

OK, so we're going to show two examples of these chain reactions. One is stable chain and the other one is unstable chain. And go through the process of how you solve for them.

So the first example is taking, so let's do a stable chain. Take acetaldehyde, CH_3CHO , that decomposes to form methane and carbon monoxide. That's the reaction. And here are the observations. There are two observations. The first one is that methane and carbon dioxide are not the only products that are formed. In fact, there's a trace amount of ethane and hydrogen, dihydrogen are also formed. That's a clue to something funny is going on here. That there's a mechanism that's more complicated than just this decomposing in a first order process.

And the other thing is that the rate, if you do an experiment and you measure, somehow you do a half time experiment, or an initial rate experiment, or one of the ways that we talked about early on, you measure the rate of the reaction and you find that it's proportional to something to the $3/2$ power. That's pretty weird. It's not a simple mechanism. It's pretty weird. And so those two observations are clues, usually, that you've got a chain reaction. The fact that you have a trace amount of extra things, that's usually due to a termination reaction. It's not a major product, it's a minor product that's the termination of the chain. And then this funny power here, in the kinetics. Of the rate of reaction, that's also usually a chain reaction.

So now we have to figure out if there's a mechanism that supports those observations. And I'm going to tell you possible mechanism that supports those observations. And you can do experiments to show that you can fish out certain intermediates. It's not proved that that's the ultimate mechanism, but it's at least consistent with these observations. More hidden chemistry.

OK, so this is the mechanism that's proposed. And then we'll figure out whether this proposed mechanism fits the data. So, the proposed mechanism is that the initiation step consists of the acetaldehyde, CH_3CHO , decomposing into a radical. Chain reactions often have radical processes also. Because the radicals love to make chains. To the methyl radical, and then the CHO radical. So this is the first step. It's the decomposition step, it's very slow. That molecule doesn't really want to fall apart. Then there's a propagation step. And that's the methyl radical plus

the acetaldehyde, your reactant, forming with the system rate k_2 . Forming CH_3CO radical, plus methane. So that is their product right here, coming out of the first step of the propagation. And then this new intermediate here, so there's this one here would be I_1 . The methyl radical. And the CH_3CO radical here, this is I_2 . And you have to use that up in the second step. CH_3CO . That decomposes on its own. Rate k_3 , to form the first intermediate back, the methyl radical, plus the second product, CO . And then this intermediate then feeds the first step back. And you've got your cycle. And every point you spit out your two products. And this could go on forever.

But it doesn't, because at some point those two methyl radicals, two of those methyl radicals can get along, can collide. And in a very easy way. So we've got a few termination steps. You can form two times CH_3 radical ethane, C_2H_6 . Rate k_4 , let's call this k_4 .

And then there are other side reactions that can happen. For instance, this radical here, which we haven't used up. That can also react. It's just sitting around, slowly building up as this thing, very slowly building up, because the first step here is very slow. You don't need very much of this methyl radical to start the chain. Then you start chewing up the reactant. But you're still building up a little bit of this guy here. This is a side reaction. It's not a termination reaction, because that radical's not involved in the chain propagation step. But that radical can react with some other species, M , and it could be any of the other species. Because it's just a chaperone. It's just a, to help this thing to decompose. CO plus H radical plus the chaperone back. And then that hydrogen radical here can itself react with your reactant. CH_3 acetaldehyde, CH_3CHO , with a rate k_6 . To form hydrogen gas plus your intermediate, CH_3CO .

And this intermediate can feed the step right here. OK, so in terms of the observations, then, we got the right products. Methane, and carbon monoxide. We've got the right amount of trace stuff, the ethane coming out from the termination step. And hydrogen gas coming out from the side reaction. And I should probably have written CO also forming from the side reaction - well, CO is a real product, so it's happening both from the side reactions as well as from the main reaction. So we've got all the species taken into account. And now we've got to show that this mechanism here, in fact, gives rise to this $3/2$ power.

And I know I won't be able to do it on one board. I want to keep all up, so let me use up.

So the first thing, as we've been doing in kinetics this whole time is, you've got to write down all your rates. Once you've got that down, and you haven't made a mistake, then you basically have the problem solved. So you write down all your rate laws. Eventually, what we're interested in showing is the rate of the reaction, is that power. So that's write down what the rate of the reaction is. The rate of reaction is the rate of formation of one of the products. Let's say the methane. So we write down that rate. How was it formed? It's formed through the k_2 step. It's formed through this step right here. Which is a second order in CH_3 radical times CH_3CHO . acetaldehyde.

We're going to keep that in the back of our mind. Because we're going to need this again. Because we want to show, at the end, that in fact this is, this rate is proportional to this funny power. There's the intermediate sitting here. So what's the rate for this intermediate here is CH_3 , dt . There are many places that it's coming from. It's being created in the first step, and so the hard part here is bean-counting. Making sure that you've found all the places where the species is being created. k_1 times acetaldehyde, CH_3CHO , and then it's destroyed through the second step, minus $k_2 \text{CH}_3$, better get your signs right also. So there's the destruction, there's the formation. Times acetaldehyde, CH_3CHO . Then it gets created again, through the second step of the propagation, rate k_3 . Radical CH_3CO . And then it finally gets destroyed in the termination step. We've got to put that in, even though it may be a very small amount compared to these other amounts there. So the termination step is k_4 . And it's a second order process, CH_3 squared.

We've got another intermediate. We want to write down all our intermediates here. Because they're all related, it's the intermediates sitting here. So there are going to be a couple of differential equations. So we've got to write down the equation for that CH_3CO radical. And again, you look at your mechanism. And you find out where it's coming from. It's being created in this step. Destroyed in this step. It's also being created in this step. But we're going to ignore that side reaction for now. Just to make our lives a little bit easier. $k_2 \text{CH}_3$. You've got to put the termination step in, but the side reactions are not so important. CH_3 . Because if you don't put the termination step in, then your reaction's just going to go on forever. That's just not physical. Minus $k_3 \text{CH}_3\text{CO}$.

Creation and destruction. OK, so now what do we do? Well, we know it's a chain reaction. A stable chain reaction. Because we don't create more intermediates than we started out with. The first step is always very slow. Initiation at this step is slow. So we're not making very much of this methyl radical. We're not making very much of it. And we're not making any more of it here. So during this whole time that the chain reaction is happening, this methyl radical here is in small quantities. Small quantities and it's not going to change very much at all. It's pretty much stationary. Magic word is stationary. Stationary means it's not changing. Not changing, so which approximation does that belong to? That's a steady state approximation. We've got a steady state here. Chain, which is going blah, blah, blah, blah, stationary. Steady state. All sounds the same. So that's the clue here. This is going to be a steady state approximation problem. So we're going to put a steady state here. We're going to put a steady state here. We're going to set this equal to zero. We're going to put a steady state right here. We're going to put a steady state here. We're going to set this equal to zero.

And suddenly the problem becomes a tractable algebraic problem. Now we have, to solve this, let's do it in one more place. Let's put it right here. So now we have two equations, two algebraic equations. Two unknowns. These two intermediates. The concentration of these two intermediates are the two unknowns. Two equations, two unknowns, we can solve it. It can be messy. But not necessarily tricky. Just turn the crank. And computers could

do this.

So, let me just write the answer. Because I don't want to go through the algebra. After you turn the crank, what you want is to get this out. You've got your two equations, two unknowns. You turn the crank. And you get that form for the concentration of the methyl radical $2k_4$. CH_3CHO turns out to be to the $1/2$ power. When you do that. There's the funny power coming up. That's going to be here. And then this is what you want to put into here. So, and there's the acetaldehyde, sitting right here. There's one acetaldehyde to the $1/2$ power, times acetaldehyde to the one power, that's the whole thing to a $3/2$ power.

So in fact, the rate is proportion to the $3/2$, according to our mechanism. And all these rate constants go into it as well. And what we find is that the rate of reaction is equal to k_2 times square root of k_1 over two k_4 . CH_2CHO to the $3/2$ power. Basically, k prime to an effective rate times that. It's a typical problem. Any questions on this one right here? Yes.

STUDENT:: [INAUDIBLE]

PROFESSOR: Here? Right here.

STUDENT:: [INAUDIBLE]

PROFESSOR: You know, according to my notes I don't have it, yes, you're absolutely right. There's a two here. Thank you very much. It's arbitrary. Where the two comes from, I didn't want to get into this. Sometimes it's a matter of convention. When you have a second order reaction, $A + B \rightarrow C$, you write your rate of the reaction, as let's write it here, k times A times B . Sometimes we have $2A \rightarrow C$. You have a rate k_2 , and the rate of the reaction is, you can write it as dC/dt , which is minus k_2 times A squared. But if you write dA/dt , because of the stoichiometry. dA/dt concentration for, so you have that C is equal to A_0 minus A , twice. So dC/dt is equal to minus two dA/dt . So minus $1/2$ dC/dt is equal to dA/dt . So dA/dt is equal to minus $1/2$ k_2 A squared. And instead of having the $1/2$ here, what we do is we redefine our rate constant. So that's k_2 prime is equal to twice k_2 . You put a two here, a prime here. Get rid of this here. And there's the two sitting right here. Purely convention. Not something to really worry about. You've just got to have it right at the beginning, and keep that two in, if you're going to put it in there. Does that make sense?

It's the stoichiometry, it's because of this two sitting right here. Then you have a choice. You can either say the rate of the reaction is the rate of formation of this thing. Or you can say the rate of reaction is the rate of destruction of A . And then if you say that this is the rate, and you don't want to have any factors in here, then the two shows up here. If you want to say this is the rate, you don't want any factors in here, then you're going to have a different rate constant. Purely arbitrary choice. Good question, though. Any other questions? OK.

So, there's another thing about the chain reactions, a bit of nomenclature that's interesting to talk about. It's the chain length. And that nomenclature is due to the fact that many of these chain reactions are used for polymer reactions. Where you use radical polymerization and then you have, basically, in a polymer reaction you'll have an initiator and then you'll add a monomer through a radical process. And another monomer will add through a radical process. Another monomer will add, another monomer will add, another monomer will add, and then you're going to terminate. And then you end up with a chain. A polymer chain. So your product, instead of being molecular products, the product is adding a monomer to the chain of the growing polymer.

And then it's meaningful to talk about chain length. So that's where the nomenclature comes from. It's a number of cycles of the reaction before you get a termination step. So we can define the chain length as the number of propagation steps per initiation step. That gives you the chain. Each one of these is a propagation step. And there's the initiation step here.

And this could also be termination step. In in a stable chain, or termination step. There's a termination step here. For every initiation step in a stable chain, you've got a termination step. Because you're not building up intermediates. So you create it. At the end of the chain you terminate it. You have as many initiation as termination steps. So you have a choice here, in the algebra. You can use either one.

So another way, instead of doing numbers here, you can also rate. This is also the rate of propagation divided by the rate of initiation. You just take the derivative of this with respect to time of the top and bottom. Same thing. So we can also define it as rate of propagation divided by rate of, let's say, termination. Or initiation, whichever is your favorite one to use to make it simple. So, for instance, in our example here, the rate of propagation is the rate, also the rate of product formation. Since we have a product formation. Rate of propagation is the rate of forming this methane here. So in our example here, the rate of forming the methane is the rate reaction here. This is this right here. So you can plug this here on top. I may not write it down because I don't want to spend time writing too much down.

So this guy goes right in there. And then the rate of termination is going to be, the rate of termination is, well, let's not use termination because that has intermediates in it. Let's use initiation. Since we have a choice. Rate of initiation. Either one works fine. Initiation is k_1 times the acetaldehyde. k_1 times CH_3CHO . So there's the $3/2$ power, which, where is it? There's $1/2$ plus, so $1/2$ plus one is the $3/2$ power here. So there's CH_3CHO to the $3/2$ power. CH_3CHO to the $3/2$ power, then some effective rate k' . And you end up with chain length going to the $1/2$ power. So there's some k'' , so effective rate times CH_3CHO to the $1/2$ power. That's the length of chain. It depends on the concentration of the reactant. And the typical chain's on the order of a couple hundred or something like this, usually. You always have a termination step at at some point. Maybe a few thousand if you're doing polymer chemistry and sometimes millions, if you're very good at doing polymer chemistry.

OK, any questions on the stable chain? OK, let's do the explosion now.

And so this is the typical example. Of an unstable chain. It's the formation of water from hydrogen and oxygen. $2 \text{H}_2\text{O}$. That's the reaction. Gas phase reaction. And the observation is that that, well, you know the observation. You put a spark in a balloon that contains hydrogen and oxygen and get an explosion. So we're going to have to account for that. Sometimes you don't get an explosion. Sometimes it kind of peters out. You have a drop of water coming out. Not bad. And there's a temperature dependence to it also. So, whatever mechanism we put in there needs to account for all the pressure dependence, the stoichiometry dependence, and the temperature dependence.

So this is the mechanism that's proposed. Initiation. You have your hydrogen molecule. Spark, or something slow that decomposes it to two hydrogen radicals. This could be a spark plug, and every time you make a little bit of the radical. Then you have a branching step. Where your radical reacts with the oxygen molecule to form a hydroxyl radical. Plus an oxygen. Oxygen atom plus your hydrogen gas, your reactant, reacts to form more hydroxyl radical plus the initial intermediate. And then the hydroxyl radical, I don't know why I have parentheses here, hydroxyl radical reacts with the reactant again, the hydrogen gas, k_3 , to form more of the initial intermediate plus water, your product.

So there are three steps to the branching here. You get one intermediate, one of the initial intermediates here coming in. Forms a second intermediate. OH radical. Two OH radicals. And the OH radicals form the hydrogen. There's also radical hydrogen that's formed right here. So you have this formation.

So because you're forming two hydroxyl radicals here, in this step here you're actually forming the equivalent of two hydrogen radicals. So, one hydrogen atom here. After going through the branching, you end up with three hydrogen radicals. So you go from one to three in one cycle. And the second time around, you go from three to nine. The next time, you go from nine to 27. Pretty soon you've got a couple of billion hydrogen radicals. And that's the problem right there. Or the opportunity. The opportunity to get something that goes out of control.

And there are termination steps. That we need to take into account. The hydrogen radical can hit the wall. Before it finds something to react with. And gets stuck. So if the pressure is low enough, you know that's going to happen. You're going to make a hydrogen radical. Hardly any gas molecules around. It's going to find a wall, it's going to get stuck. It's very reactive. So that's going to terminate the process. Hydrogen radical could re-find an oxygen and another chaperone, that's a termolecular process. That's an unlikely process. But nevertheless, it could happen. With another termination step, to form the HO_2 radical plus M. And then that HO_2 too radical can react in a side reaction to form some products, but not be part of the chain. Yes.

STUDENT:: [INAUDIBLE]

PROFESSOR: How do we get three hydrogens? Because there are two hydroxyl radicals here. And so in this step here, you actually have two hydroxyl radicals to form two, so I could multiply this by two. But you usually don't do that.

So this already tells you what conditions you're going to get, with something where the termination is fast, compared to the propagation. Because you have low pressure. If you can't get that hydrogen radical to react with something before hitting the wall, you're going to be OK. You're not getting an explosion. This tells you that a very high pressure, where the probability of having a three-body collision becomes high enough, then you're going to terminate the chain as well. Those hydrogen radicals are going to find oxygen molecules and some other molecule and form this radical before you propagate the chain. At least some reasonably high pressure. So that's the clue here.

What's the strategy? The strategy is to assume that everything's going to be fine. That is, stable. That's going to be the strategy. And then we're going to do a proof by contradiction, basically. We can assume that the chain is stable. That we can use the steady state approximation. We're going to apply the steady state approximation. We're going to find where that breaks down. And where it breaks down means that it wasn't right. That the intermediate concentration was too high. And that means that we're going to get an explosion. That's the logic. So strategy is a proof by contradiction, basically. Proof by contradiction.

So we're going to assume that the propagation, or the intermediates, are in small quantities. We're going to assume that we can use the steady state approximation, the $d[O]/dt$ steady state is equal to zero. That the hydroxyl radical, $d[OH]/dt$, steady state is equal to zero. And that $d[H]/dt$ steady state is equal to zero. These are going to be our assumptions. That all the intermediates are in small quantities. And they don't change very much.

And now we're going to write down, you write down the rates that correspond to these guys. And then you solve. So I'm only going to do this first one here. So you write dO/dt , you see where it gets formed. It gets formed in the first step here. So it's going to be k_1 times H radical times O_2 , and it gets destroyed in the second step here, minus k_2 times O times H_2 . You set the steady state approximation, you get a steady state. Steady state here, you set that equal to zero. You solve for O, radical O, steady state. And you find that it's k_1 times H times O_2 times k_2 H_2 .

Then you do the same thing for the other radicals. You solve for OH steady state. And you get some expression which is in the notes. I'm not going to write it down, it's going to get too messy. But the expression that I will write down is the final expression, which we're going to be taking into account.

So, this expression here, for the oxygen atom. It has the radical in there. So it's not, we'd like something that's just in terms of the rates and either products or reactants. And this hydroxyl radical, the concentration turns out, it will also be a function of the concentration of the hydrogen radical. So what we really want, I don't want to cover this up, let me go on this board here. So when you solve for this, the hydrogen atom is where you get something that's free of intermediates. And has just rates in it. There's a termination rate here going in the denominator. Another termination rate in the denominator. Times O_2 times M , where M could be anything, really. Minus, and there's the creation rate of the first propagation step. O_2 here.

So now we have to see whether or not our approximation was valid. We made an approximation. We said the steady state approximation was valid. If it is valid, then this concentration, this pressure here, needs to be small. Needs to be small at all times. If it's not small, then steady state is not valid, we have a branching non-stable chain and we've got an explosion.

So let's look at the different possibilities here. What are the possibilities? Well, the first possibility is that as we saw intuitively, when we wrote down this equation here, the first possibility is that we're at low pressure. Where at low pressure, then, k_1 times oxygen is very small. Because the concentration of oxygen is small, the pressure is small. k_5 times the pressure of oxygen times the pressure of M is small also. So $k_5 T O M$, O_2 times M is small. And they're both, then, much smaller than k_4 times the time. k_4 termination. The hydrogen radical hits the wall before finding anything else. End of chain.

So in the equation here, these two guys are small compared to here. R_i , the initiation rate, is very small. You control that by your spark. Once a second, once a minute. Could be really, slow. Steady state is good.

We don't have an unstable chain. No explosion here. Medium pressure. You've got a medium pressure where two k_1 times oxygen concentration is approximately. You're building up your concentration. This is getting bigger here. This is a constant. This is getting bigger. This is also getting bigger, but you've got this rate here and this rate here. At some point, at some point, this rate here, two k_1 times oxygen concentration, is going to be on the order of $k_4 T$ plus $k_5 T$ times oxygen times M . At some point it's going to be like that. And then you're in big trouble. You're in big trouble, because you've got a denominator here that's really tiny. Could be even, if you hit it right on the nail, you get zero in the denominator and then you're in real trouble from the math perspective. But from the physical science perspective, it's not being in trouble. Is just that your approximation is wrong. The approximation that you were in a stationary state was wrong. And so that means that in this case here, if you want to have an explosion, you've got it. So you adjust everything until you're in a situation. And then finally, you keep increasing the pressure. And then if you increase it high enough, then this guy here, which goes as the square of the pressures, is going to overwhelm this. Which goes linearly with pressure. And k_5 , the termination step, O_2 times M , is going to be bigger than two k_1 times the pressure of O_2 .

And then you've got something small again. This is where that's hydrogen radical here is able to undergo a termolecular process before finding a reactant. Then steady state is valid. OK. At very high pressures, you get in trouble again, because this hydroxyl radical, this HO₂ radical, so at very high pressure. then what happens is that you have this side reaction, HO₂ radical plus hydrogen goes to H₂O plus hydroxyl radical. So there's a probability that this radical here finds a hydrogen molecule. And then feeds into the propagation through this hydroxyl radical that's the result. And then that keeps the chain propagating. So at very high pressure, you're in trouble again. And you get an explosion again.

So you can plot this as a function of the pressure. And we're going to put pressure, actually, on the y axis here. Let's put pressure here. Put temperature here. And so for a given temperature, let's call it temperature T prime, at low pressure there's no explosion. Then there's a range of pressures. Where there's an explosion. Medium pressures. And then a high pressure termination wins again. And then if it's really high you get explosion again. You do this for, as a function of temperature. And what you find that is a diagram, looks like a phase diagram, that looks something like this. Where at high temperature, you get an explosion at low temperatures, and this steady state is valid.

OK, any questions on this? Don't try this in your kitchen. Go to the desert if you want to do this. Or don't do it either. OK.