

**Combustion in Air Breathing Aero Engines**  
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**Lecture - 04**  
**Chemical Kinetics – I**

Hello friends, welcome back. So, today's module is about Chemical Kinetics.

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**Module 2**

**Chemical Kinetics**

- i. Theories of reaction rate
- ii. Chain mechanisms

Majority of the material is taken from

- i. Combustion Physics by C. K. Law, Cambridge University Press.
- ii. Combustion (4<sup>th</sup> Edition) by I. Glassman, Elsevier.

And we will be looking into the different theories of reaction rate, and chain mechanisms. And the majority of this material is taken from Combustion Physics by Prof. C K. Law and Combustion by Prof. Irvin Glassman.

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**Introduction**

1. **Chemical thermodynamics:** Relates the initial to the final equilibrium states of a reactive mixture; does not distinguish the path and time in the process
2. **Chemical kinetics:** Describes the path and rates of individual reactions and reactants; can be extremely complex -  $10^3$  intermediates and  $5 \times 10^3$  elementary reactions.  
How does the mixture get from the initial to the final state? How long does it take?

So, what did we learn last week, last week we learned about chemical thermodynamics. What did chemical thermodynamics tell us, chemical thermodynamics related the initial and final equilibrium states of a reactive mixture that is if you are given a reactive mixture methane and here and it will tell you what will be the concentration of the different products like  $\text{CO}_2$ , water, carbon monoxide if it is formed, hydrogen if it is formed. But you see it did not tell you about which path it took. Why the path is important, it will become apparent in a very short amount of time and the time it took for the process to happen. It just tells as you know in the thermodynamics, thermodynamics does never tells you about the path it tells you about the initial and the final states. Often as you we will see the path of the process is very important and that is where chemical kinetics comes in.

Chemical kinetics described the paths and the rates of the individual reactions and reactants. Now, you might think that what are this individual reactions and reactants. When you talk about hydrocarbon combustion or hydrogen combustion, hydrocarbon or hydrogen does not become water or carbon dioxide respectively as this might be in one-step. The hydrocarbon fuel breaks down into small components, and it undergoes numerous elementary reactions before it can become products carbon dioxide and water and as such these paths can be very complex.

As you see here there can be up to  $10^3$  intermediates formed for a large hydrocarbon molecule which happens practically for example, you say you consider kerosene or you consider gasoline, you consider diesel, you consider biofuels the combustion of these can involve up to 1000 intermediates and 5000 elementary reactions or even larger. This is just some prototype numbers it can go even larger.

So, there is. So, a such combustion never happens combustion reaction never happens in one step it happen through a series of steps through a series of reactions and as you will see that these series of reaction that are involved often this reaction happen in series of in the parallel and the series of reactions and the species that are involved they have different times associated with them they do not have similar times. So, as a result of this, chemical kinetics become very important it tells you how does the mixture get from the initial to the final state and how long does it take. So, this is the thing.

Now in the introductory session itself we told that combustion essentially rests on two pillars chemical kinetics and fluid mechanics. So, as you understand chemical kinetics is very important. Now, you can argue that I am a combustion engineer. Of course, I want to design an engine, do I should I know about chemical kinetics? The answer is yes. Let us consider that what are the steps involved in designing a new engine. If you are engineer if you work alone or you work in a team suppose you are designing a new engine, first will you do a 1-D analysis right in the 1-D analysis suppose your designing a gas turbine engine you will do a 1-D analysis of the different components of the different parts. You will do analysis in the thermodynamic analysis and fluid analysis in the intake in the compressors, in the combustor, in the turbine, in the nozzle.

In the combustor first you will if you are doing a 1-D analysis you are involved in gross numbers you will do like consider the combustor like a black box. You will consider air entering, you will consider fuel entering and you will be interested to know what is the temperature of the exit flow and the composition of the exit flow right of course, that is very important. And that comes as you see I have seen from the previous lecture these question that what will be the approximate temperature of the exit flow and what will be the composition of the exit flow this can be answered by the chemical equilibrium considerations. Adiabatic flame temperature and associated heat of formation and heat of combustion will tell you the approximate temperature of the exit flow and the equilibrium calculations will tell you about the composition of the exit flow.

But now, you want to refine your analysis this is just a 1-D analysis you cannot design an engine into or a combustor as such just by 1-D analysis, suppose now you will go to a CFD analysis. You can use your own code if you have or you can use a commercial code or you can use a research code to design the combustor. So, now, here in the combustor you will consider this all the governing equations which will come later that is the flow equations which is basically conservation equations, mass balance, momentum balance, energy balance and you will have to consider the reaction mechanisms.

Reaction mechanisms are nothing but it is a description a comprehensive description of chemical kinetics. So, you see to even nowadays, you have to design an engine at a very at a sophisticated level you want to know how you are basically you want to predict or you want to ensure while yet the design phase itself that the combustion will be stable whether the flame that you will get inside the engine, whether that can be stabilized that all in the combustor or not. Whether that can be ignited at all or not whether it will blow of or not it will just lift go away from the combustor or not.

To predict and to ensure this will be reasonably satisfied these properties that you will have stable combustion inside the combustor which is very necessary for power generation inside the engine. You will need to incorporate all this reaction mechanisms into the flow. Now, the reaction mechanism that will incorporate can be of different levels of complexity, but at least it has to be there in some form; otherwise you cannot do a combustion calculation.

So, inherit in the combustion calculations, you do whether you are an engineer whether you are a scientist or a mix of both, chemical kinetics is an integral part of combustion. So, please pay attention to this lecture today. And we will discuss different aspects about chemical kinetics that how do you describe kinetics, what is the different what is a reaction rate, what are the properties or what are the parameters does reaction rate depends on, how can the reaction rate be connected to the consumption rate of a different species.

And then the reaction rate involves several constants, how do you even can estimate those constants, what are the theories that goes into this constant, those will be discussed. And then we will discuss some basic generalized reactions that happen in combustion and we will finish with some topics on how you can measure actually those reaction rates

in the laboratory. So, today's lecture is very important and forms a very important part of this series of lectures on combustion in air breathing aero engines.

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**Outline**

1. Phenomenological law of reaction rates:  
Dependence on temperature and concentration
2. Theories of reaction rates – The Arrhenius law:  
Collision theory, transition state theory
3. Chain mechanisms: Straight and branched

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So, as I said this is outline will talk about the phenomenological law of reaction rates. How does it depend on what are the parameters it depends on as you will see. It depends on essentially temperature and concentration. And of course, concentration can be shown to depend on other things like pressure etcetera. And then you will have theories of reaction rates we will have the Arrhenius law, and how in the Arrhenius law the parameters that goes in to Arrhenius law, how they can be estimated by collision theory, transition state theory. And then we discuss chain mechanisms straight and branched that are what makes this is we will see that this branching of this chain carriers of the chain mechanisms is will is the thing that makes combustion a very unique chemical phenomenon.

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### Law of Mass Action

- For a single-step forward reaction:

$$\sum_{i=1}^N \nu_i' M_i \xrightarrow{k_f} \sum_{i=1}^N \nu_i'' M_i \quad \text{H} + \text{O}_2 \xrightarrow{k_f} \text{OH} + \text{O}$$

*Reactants*                      *Products*

<i>i</i>	<i>M<sub>i</sub></i>	<i>ν<sub>i</sub>'</i>	<i>ν<sub>i</sub>''</i>
1	H	1	0
2	O <sub>2</sub>	1	0
3	OH	0	1
4	O	0	1

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So, first things first, kinetics has to begin with the law of mass action. Now, for a single step forward reaction that is this can be true for any reaction as such. Any reaction this is once again if you remember from the previous class, this is a generalized description of a chemical reaction, these are the reactants as you will see, and these are the products. And the rate at which this reaction happens this is the first time we are introducing this quantity. We will see what this rate constant essentially which is called the rate constant of this reaction for the forward reaction as such is given by  $k_f$ . Now, as I said this is a generalized form. So, if you remember I will show you this to once again because it is very important to understand what this generalized form represents and what are these different things represents. Because we will be using this will be building the entire of today's lecture based on this consideration of this generalized form of the reaction representation.

So, please pay attention to this. These are the stoichiometric coefficients, this  $m$  is the species name, this is the stoichiometric coefficient on the product side, and this is the species name once again. So, when you write,  $i$  is equal to 1 to  $n$  it actually 1 to  $n$  goes from it considers all the species that is possible in the system. So, it contains both reactants species as well as the product species. Just to give an example, this is your specific reactions that you are interested in H plus O<sub>2</sub> goes to OH plus O. Now, I keep on writing this reaction there is one more reason as you will see later in later class that this is most important reaction in hydrocarbon oxidation this is the most important

combustion reaction. So, that is why I keep on writing this, this will be then we will also develop feeling for this and we will discuss things terms of this.

So, suppose this is the reaction we are interested in and this is the  $k_f$  is a rate constant of that reaction. So, then if you see here the  $\nu_1$  then if you just tabulate this things once again, say this is  $\nu_i$  first let me say that this is  $i$  this is  $m_i$  and this is  $\nu_i$ . So,  $i$  is basically 1, 2, 3, 4 why  $i$  goes from 1, 2, 3, 4 here four is equal to  $n$  as you see because you see there are 1, 2, 3, 4 - four species involved. So,  $i$  goes from 1 to 4;  $m_1$  is H,  $m_2$  is O<sub>2</sub>,  $m_3$  is OH and  $m_4$  is O, and all this  $\nu_i$  are essentially 1, 1, 1, this is 0 because on the reactant side the stoichiometric coefficient of OH and O is 0. So, actually this is essentially  $\nu_i$  dashed and  $\nu_i$  double dashed is this is 0, this is 0, this is 1, and this is 1.

So, these are how you essentially represent generalized reaction. Because you see I mean there is no point writing that there will be two species, there will be three species typically  $n$  goes from 1 to 4 or typically goes typically  $n$  is essentially 4 or 5 in a order or six in a in normally in hydrocarbon reaction mechanisms. But we need to right it in a generalized manner because otherwise as you will see we cannot make the equations that will arise be very clear.

And this is also as I said before that this is also the way like modern combustion literature or manuals of different course are represented in this form. So, it is important for you to familiar get familiar as to with this kind of representations, but with this now it should be clear what I am meaning by  $\nu_i$  dash,  $\nu_i$  double dashed and  $i$  and  $m_i$ . So, let us erase this, but if you are not yet clear just spend a minute with yourself and just think about it will be clear in a given second, but this is very important because as I said that all this is the foundation and all the later analysis will built on this.

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### Law of Mass Action

- For a **single-step** forward reaction:
 
$$\sum_{i=1}^N \underbrace{v_i'} M_i \xrightarrow{k_f} \sum_{i=1}^N \underbrace{v_i''} M_i$$

Reactants
Products
- Molar rate of change:
 
$$\hat{\omega}_i = \frac{dc_i}{dt}, \text{ units of } c_i: \text{ moles/unit volume}$$
- $i$  and  $j$  are related by:
 
$$\frac{\hat{\omega}_i}{(v_i'' - v_i')} = \frac{\hat{\omega}_j}{v_j'' - v_j'} = \omega, \quad \text{Reaction Rate}$$

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So, now we can define molar rate of change that is a rate of change of the concentrations of the species  $i$ , which can be consumption or generation or production rather. So, this  $\hat{\omega}_i$  is the rate of change of the concentration of species  $i$  is the rate of change of the production of the species  $i$  this  $\omega$  essentially represents the rate of change of the concentration of species  $i$ , which can be consumption or it can be production.

Now, this is not reaction rate please keep in mind, this is the rate of change of concentration of a given species, but of course, you can connect this to the reaction rate and this is how you connect it. This is because as you have seen before that the rate of change of species  $i$  and species  $j$  in a given reaction are connected to this relationship and because this is true for any species  $i, j$  inside in the reaction mechanisms. This can be represented by this generalized  $\omega$ , which you see does not have  $\omega_i$  or  $\omega_j$  and this is the reaction rate. So, please understand the difference. This is the rate of change of the concentration of species  $i$ , this is the reaction rate these two are not quantities, but they are proportional and the proportionality constant is given by the change of the stoichiometric coefficient between the product side and the reactant side. So, please keep these things in mind.



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### Law of Mass Action

1. **Law of mass action:** Reaction  <sup>$\omega$</sup>  rate is proportional to product of concentrations; scaled reaction rate given by

$$\omega = k_f(T) \prod_{i=1}^N c_i^{\nu_i}$$

$\omega_b = k_b(T) \prod_{i=1}^N c_i^{\nu_i}$

2.  $\omega$  is proportional to collision frequency which is proportional to the product of species conc.

2. **Proportionality constant  $k_f(T)$ :** Reaction rate constant; **primarily function of temperature**

$$k_f(T) = B T^\alpha \exp\left(-\frac{E_a}{R^0 T}\right)$$

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Now, with this information, we can come to the law of mass action which says the most important thing that is reaction rate which was our omega is proportional to the product of the concentrations. And scaled reaction rate is given by a reaction rate constant which is the function of temperature. And this capital pi is essentially a continued product from i equal to 1 to N and it is a continued product on the concentration of the species i with an exponent of nu i dashed, but note this is nu i dashed only. So, this nu i dash is very important because this nu i dash is non zero only when you are considering reactants; nu i dashed is equal to 0, if you are considering product.

So, the reaction rate is only dependent on the concentration of the reactants which appears on the left hand side. But then do you mean that we do not consider the products at all, no, it is not that. If you are interested in finding the reaction rate of the backward reaction this is essential the reaction rate of the forward reaction then you can write it like this the reaction rate of the backward reaction is given by this way. This is the backward reaction rate constant times this product is equal 1 to N c i nu i double dashed. Of course, at equilibrium, your rate of the forward reaction and the rate of the backward reaction will be same. But here you see that the reaction rate is equal to the product of the concentrations of the reactants raise to their stoichiometric constants.

Now, this is because there is a reason to it. Though it is phenomenon logical it is found out phenomenon logically, but there is a reason is that. The reason is that will come also

this later that essentially it comes from a macroscopic view point where you think that this reaction rate constant is essentially proportional to collision frequency. And of course, the collision frequency can be considered to be proportional to the product of the species concentration, the more species you have the more chance is that there will be more collision of that species involving that species.

So, there is one this comes, but we will arrive at this in a very rigorous way using two theories. So, we will not discuss too much about this at this state, but please keep in mind this formula this is I mean if you are involved in combustion in any form, this is definitely 50 percent of combustion kinetics. Now, proportionally constant  $k_f$  what does  $k_f$  depend on,  $k_f$  is essentially a reaction rate constant, and it is primarily a function of temperature. And this temperature dependence is given by this these are constant  $B$  times the  $T$  to the power of  $\alpha$   $e^{-E_a/RT}$ ,  $E_a$  is you called your activation energy. And  $R$  zero is universal gas constant, and  $T$  is of course, the temperature will come to this later. This is just for the sake of completeness we are defining  $k_f$  here.

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**Law of Mass Action**

Example:

$$\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$$

$\hat{\omega}_{\text{H}} = \hat{\omega}_{\text{HO}_2} = \omega$   
 $\hat{\omega}_{\text{H}} = \frac{d[\text{H}]}{dt}$   
 $\hat{\omega}_{\text{HO}_2} = \frac{d[\text{HO}_2]}{dt}$   
 $\hat{\omega}_{\text{OH}} = \frac{d[\text{OH}]}{dt}$

$\omega = -\frac{d[\text{H}]}{dt} = -\frac{d[\text{HO}_2]}{dt} = \frac{1}{2} \frac{d[\text{OH}]}{dt}$

$\omega = k_f [\text{H}][\text{HO}_2]$

$\omega = k_f(\tau) \prod_{i=1}^N C_i^{\nu_i}$   
 $= k_f [\text{H}]^1 [\text{HO}_2]^1$

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Now, let us give the example of another one again H plus HO<sub>2</sub> goes to H plus OH. So, then I can find out what is  $\omega_{\text{H}}$  and that will be given by that will be essentially related to I can say that this is 0 minus 1 is equal to  $\omega_{\text{HO}_2}$  0 minus 1. 0 is my  $\nu_i$  double dashed, 1 is my  $\nu_i$  dashed, this is my  $\nu_j$  double dashed, this is my new  $j$

dashed and this is equal to reaction rate. And this is this guy is of course, the rate of change of species H and that is equal to  $\frac{d[H]}{dt}$  and if I substitute it here and then consider this and this and this is what I can. So, if I just have simplify I can right from here  $\frac{d[H]}{dt}$  minus of  $\frac{d[H]}{dt}$  is equal to  $\omega$  is equal to minus of  $\frac{d[HO_2]}{dt}$  and that is given by this  $\omega$  is equal to  $k_f$  times H times  $HO_2$  because this is the law of the mass action.

So, if you remember  $\omega$  is given by the in the generalized form is given by  $k_f T$  times this one product of  $i$  is equal to 1 to  $n$   $c_i$   $\nu_i$  dashed  $c_i$  is the concentration of the  $i$ th species. So, for  $i$  is equal to 1 my  $c_i$  is essentially H; for  $i$  is equal to 2, my  $c_i$  is essentially  $HO_2$ . So, we get  $k_f$  times H  $\nu_i$  dashed is equal to 1. this is I can write as 1, I can write as 1. So, this is raise to the power 1 as raised and this what we get. You should consider any other reaction that you know and find out using the law of mass action what should be the reaction rate for that reaction.

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### Law of Mass Action

Example:

$$H + HO_2 \rightarrow OH + OH$$

$\hat{\omega}_H = \hat{\omega}_{HO_2} = \omega$   
 $\hat{\omega}_H = \frac{d[H]}{dt}$   
 $= -\frac{d[H]}{dt}$

$$\omega = -\frac{d[H]}{dt} = -\frac{d[HO_2]}{dt} = \frac{1}{2} \frac{d[OH]}{dt}$$

$\omega = k_f [H][HO_2]$

**Question:** What is the expression for the backward reaction?

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Now, what is the expression for the backward write reaction that is the question? We can also try to estimate that and we will come to this question later.

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**Reverse Reactions**

Every **forward reaction** has a **backward reaction**:

$$\sum_{i=1}^N \nu_i^f M_i \xrightarrow{k_f} \sum_{i=1}^N \nu_i^r M_i, \quad \sum_{i=1}^N \nu_i^r M_i \xrightarrow{k_b} \sum_{i=1}^N \nu_i^f M_i$$

Net reaction rate:

$$\hat{\omega}_i = \hat{\omega}_{i,f} + \hat{\omega}_{i,b} = (\nu_i^r - \nu_i^f)(\omega_f - \omega_b) = (\nu_i^r - \nu_i^f)\omega,$$

$$\omega = k_f \prod_{i=1}^N c_i^{\nu_i^f} - k_b \prod_{i=1}^N c_i^{\nu_i^r} \quad \downarrow f(K_c)$$

$\omega_f \quad - \quad \omega_b$

So, as you see that every forward reaction must have a backward reaction. And when there is chemical equilibrium the forward reaction and the backward reactions are essentially constant are essentially equal. So,  $k_f$ , so  $\omega_f$  minus  $\omega_b$  equal to 0 if there is a backward reaction. So, then the net reaction rate as you see here is given by this is for a given species, we can essentially write the rate of change of a given species  $i$  is given by  $\omega_i$  cap. And it is the rate of change of the species  $i$  is contributed by both the rate of change of the species in the forward reaction as well as in the backward reaction. So, these are the two contributions and then if you summarize these two things if we sum these two things we arrive at this formula.

And then we are give a left with we can find out the complete reaction rate for a reaction which involves both forward and backward reactions and this is given by this things. So, we can say that this is the forward part and this is the backward part. And this is the net reaction rate and of course, this is equal to 0, when you have chemical equilibrium. So, at chemical equilibrium as I said that  $\omega$  is equal to 0.

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**Reverse Reactions**

- At equilibrium:  $\omega \equiv 0$   
$$\frac{k_f}{k_b} = \prod_{i=1}^N c_i^{(\nu_i'' - \nu_i')} = K_c.$$
- Implying:  
$$\omega = k_f \left( \prod_{i=1}^N c_i^{\nu_i'} - K_c^{-1} \prod_{i=1}^N c_i^{\nu_i''} \right).$$
- Irreversible reaction approximation:  
$$\omega \approx k_f \prod_{i=1}^N c_i^{\nu_i'}$$

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So, we can basically set this to 0 and bring this  $k_f$  and  $k_b$  on the same side. And when we take the ratio of  $k_f$  and  $k_b$  we find we are left with this thing the  $i$  goes the product goes from 1 to  $n$ ,  $c_i$  raise to the power of  $\nu_i'' - \nu_i'$  which is nothing, but or equilibrium constant  $K_c$  in terms of equilibrium constant in terms of concentration which is nothing but  $K_c$ . And of course, you can have a relationship between  $K_p$  and  $K_c$  also.

So, for this we can essentially now replace this as a function of  $K_c$   $k_b$  because normally it is difficult to estimate the reaction the backward reaction rate, but it is much simpler to find out the  $K_c$  because those are mainly tabulated. So, using the forward reaction rate and using the  $K_c$  value, you can find out the net reaction rate for a given reaction. Now, if it is so that you are backward reaction is happen at a very, very small rate which is often the case same kind of branching reactions where which produces radicals. So, collision between radicals is kind of not very provable.

So, in those cases in cases of like branching reactions, you can safely neglect the backward reaction rate and in that case you are only left with  $\omega$  is equal to  $k_f$  times product goes from  $y$  is equal to one to  $n$   $c_i^{\nu_i'}$ . So, this is about the reactions.