Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 6
Chemical Kinetics 2

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We take it as axiomatic that atoms and molecules cannot react unless they collide with each other and we are primarily looking at chemical reactions you try to emphasize this all the time, so essentially we are looking at electronic exchanges and not going all the way down to the nuclei of course there are exceptions to situations.

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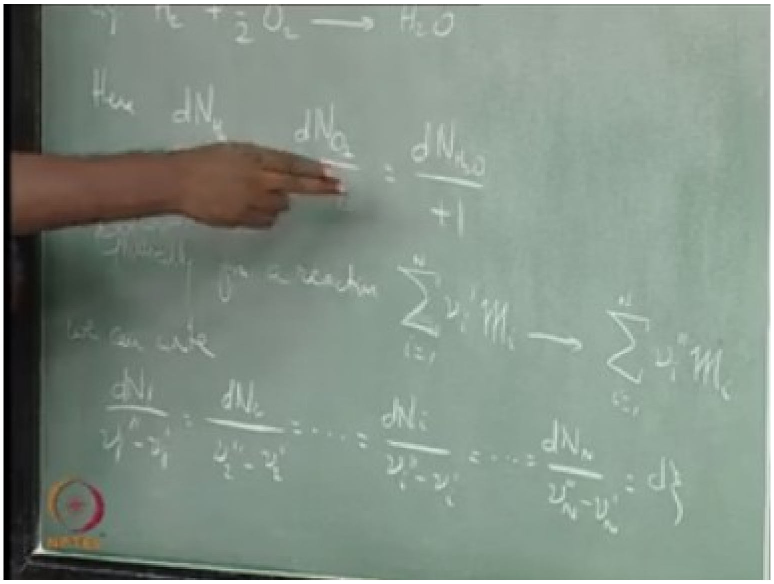

Like where we have to have molecules and atoms collide with each other you could have thermal the thermal reactions that are sensitive to temperature or in thermal response like decomposition thermal decomposition or you could have photosensitive reactions and so on, okay so let us now look at what is called the law of mass action we will just proceed systematically here so as an example if you now take the hydrogen oxygen reaction, so we can now think about a change in the number of moles of hydrogen.

In terms of a decrease and therefore we have a negative 1 could be equal to a change in the number of moles of oxygen divided by a negative1/2 because for every 1 mole of hydrogen that decreases we have only half a mole of oxygen that decreases and that could be equal to then the change in the number of moles of water divided by +1 to indicate that this is a gain a supposed to a loss what other two, so the sign and the value in the denominator for these are actually derived from whether they are reactants or products and you could also.

Now look at what is the loss relatively speaking one mole of hydrogen is lost with our mole of oxygen that is lost to produce one mole of water, so that is what that is what we write, so if you now consider a general reaction like in algebraic form that we have considered before except we now write new I single prime script mi gives σ = 1 and μ I double prime script mi, so previously we had a ni single Prime and an ni double prime we have switched to μ I suddenly we became Greek yeah there is a reason for this.

We will now get into the difference between what is called as a order of the reaction and molecularity of the reaction, so if you are now thinking something like half it refers to something like number of moles, but if you are looking at a reaction that is happening at the molecular level you cannot have like half a molecule react with another molecule giving and looking at molecules and atoms colliding with each other right.

So half a molecule cannot react as if it is half-hearted or something like that right so a molecule reacts in molecule reacts, so we will try to make the distinction over there, but as far as what we are doing now since we have 1/2 here you could stick to our notion of number of moles for the coefficients here ok which could be now taken care of by a new I single prime and a new I double prime as before which was done by ni is single Prime and I double Prime and if you want to now write a set of equations like this is actually a set of equations is that a set of three equations for three reactants three species there.

So similarly you could for n species you could now write an equations right and the way we would do is since we have actually accounted for all the n species on either side with a it is new I single Prime and a new I double Prime and we know that if something is a reactant the new I single Prime is nonzero and the new I double prime is 0 and if something is a product it is new I single prime is 0 and new I double prime is nonzero, so taking that into account you simply have to take its double prime.

Minus its single Prime to get you the right sign as well you can get a negative sign if this is 0 and that is nonzero okay you get a positive sign if this is non zero and this is zero it does not have to be exactly zeros as well you could have like excess reactant excess reactant that goes to the product side which will be a fair lesser value interms of a metric coefficient then on the right hand side then you get a positive well, so negative value here as well okay.

So all that stuff will be taken care of by this notation and then what do you do with all these things that are equal to each other okay, so we now say all these things that are equal to each other could finally be equal to a elemental change in a in a in a quantity called sigh yeah, so we now say this is equal to dxi where work.

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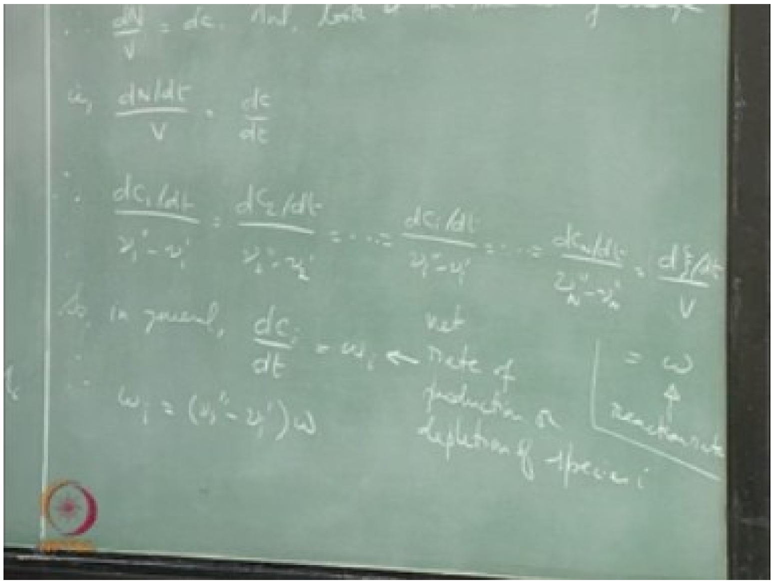

$\therefore \frac{dN}{V} = dc$. And, look [illegible]

i.e. $\frac{dN/dt}{V} = \frac{dc}{dt}$

$\therefore \frac{dc_1/dt}{\nu_1'' - \nu_1'} = \frac{dc_2/dt}{\nu_2'' - \nu_2'} = \cdots = \frac{dc_i/dt}{\nu_i'' - \nu_i'} = \cdots = \frac{dc_N/dt}{\nu_N'' - \nu_N'} = \frac{d\xi/dt}{V}$

$= \omega$ ↑ reaction rate

So, in general, $\frac{dc_i}{dt} = \omega_i$ ← net rate of production or depletion of species i

$\therefore \omega_i = (\nu_i'' - \nu_i')\omega$

Refers to ζ reference ζ refers to degree of advancement, advancement of the reaction right so it tells you how much of the reaction has proceeded depending upon how much elemental change in the number of moles has been affected for each of the species okay, so now you divide the divide the above equation by volume that means you now look at whatever is happening for unit volume V right, so nth over V is equal to C which is the molar concentration bullet concentration therefore dN over V is equal to dc.

And look at the time rate of change right that is to say dN over dt per unit volume is essentially DC over dt right, now this is very significant here ultimately what we are looking at is the rate of change the time rate of change of concentration of a species of any species okay, so of course when you are now saying n it means the total number total number of moles but you could if you put a subscript I that refers to the number of moles of species I yeah so you could do the same thing for any of those therefore we can.

Now do this for all of these that means we divide the entire set of equations by volume and then take the time rate of change in each case then you now get dC1 over dt divided by μ 1 double prime - μ 1 single prime equals dC 2 over dt divided by μ 2 double prime - μ 2 single prime etc.

For the general case of the ayats species dci over dT divided by μ I double prime - μ is single prime up to dc n over dt divided by μn double prime - μ a single prime μ and single prime, so what happens finally right, so you now have a dxi over dt divided by volume right so, so you now have so this is what we would like to call as ω which stands for the reaction rate right in that sense the reaction rate is a term that is common to a reaction all right it is you know give it you are given a reaction.

That means it will have a reaction rate okay what is it the rate off or what are we trying to measure out of this actually, it is something that is common to all the species strictly speaking what we should be asking or be interested in is what is the rate of production or depletion of a particular species okay, that is given by dc1 / dt dc2/dct etc. And therefore dc1 by dt will be μ1 double prime - μ 1 single prime time ω and so on for each of those species right so that is so you have like a common quantity reaction.

Rate from which you will now get the rate of production or depletion of the individual species that is how we try to go about doing this, so what does this really mean it is essentially a volumetric time rate of change of the degree of advancement of the reaction, so that the reaction rate essentially means at the rate of change if the degree of advancement of the reaction per unit volume so keep in mind there are two things about a reaction rate this is very, very important for you to think about all the time whenever you are bringing in reactions in the picture the reaction rate is coming it is going to come into picture and correspondingly the rate of production or depletion of individual species.

It is always per unit time per unit volume okay its volumetric rate volumetric means per unit volume rate means per unit time, okay so these two things are always there and typically in SI units if you are interested in putting this in things like mass balance and so on we are always looking at measuring this interms of kilograms per second per meter cube right that is what we are we are looking at they are beginning to look at the moment of course we are now having a Omega here which is essentially looking at the change in the number of moles per unit time.

So this is moles per unit time per unit volume and so on it is not yet kilograms right so the means we have to now throw in a molecular weight, so you cannot do that for a common reaction rate the reaction rate that is common to all the reactions you could do so for the individual species because individual species will have individual molecular weights, so you can throw in molecular weights for individual species to convert the rate of change of number of moles of those species to the rate of change of mass.

Of those species right that is what we will do ultimately but I am just trying to tell you what is all coming ahead and what are the important things that we have to keep thinking about, so if you know keep that along with that line, so in general we can say dci I over dt if this is actually ωi this is the rate of production or depletion should in fact we should say net rate of production depletion of species I write species I net rate of production of I will explain why we are saying net in a few minutes.

Essentially what you are thinking is not just one reaction here will now try to have a sequence of reactions in which a species could be produced in one reaction it could be consumed in another reaction okay, so there is like a net rate of production a depletion so that that is what that is what they were net would mean and we will see this a little bit more explicitly, but essentially what we are now saying is therefore ωi is μi single prime double prime - single prime times ω okay.

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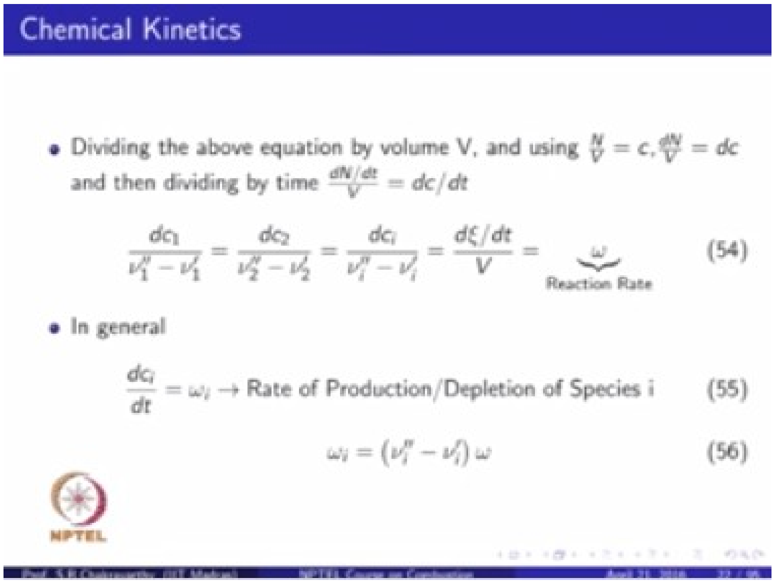

Chemical Kinetics

- Dividing the above equation by volume V, and using $\frac{N}{V} = c, \frac{dN}{V} = dc$ and then dividing by time $\frac{dN/dt}{V} = dc/dt$

$$\frac{dc_1}{\nu''_1 - \nu'_1} = \frac{dc_2}{\nu''_2 - \nu'_2} = \frac{dc_i}{\nu''_i - \nu'_i} = \frac{d\xi/dt}{V} = \underbrace{\omega}_{\text{Reaction Rate}} \qquad (54)$$

- In general

$$\frac{dc_i}{dt} = \omega_i \rightarrow \text{Rate of Production/Depletion of Species i} \qquad (55)$$

$$\omega_i = \left(\nu''_i - \nu'_i\right) \omega \qquad (56)$$

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So where are we are supposed to within this framework we should now be able to write out the law of mass action, so the law of mass action.

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The law of mass actually states that right I am not going to write long sentences like you go through in high school that is a difference, now states simply that ω equal to Ki= 1 to n ci to the new I single prime, this is what you have actually learned in high school okay now it is all put in algebraic form so this simply means that the, so on this there you say new at single prime as the exponent over there to see I what it simply means is the rate of reaction the common quantity for all the species.

That are participating in a reaction yeah it is equal to a what is called as a rate constant or a specific rate constant okay it is not a constant, we will now expand on that a little bit more time but it is like a proportionality constant, so effectively you are saying the rate of reaction is proportional to the concentrations of the reactants raised to their stoichiometric coefficients right, so when he say reactants that means you are looking at new I single Prime keep in mind you are taking like a product of all the all the species.

So if some of the species are actually products the new I single Prime's for them will be 0 therefore they do not really contribute you now have C_i to the new my single prime for them to be equal to 1 and therefore you do not have to worry about it yeah so it is pretty general expression there and the next thing that I would like to point out is K here.

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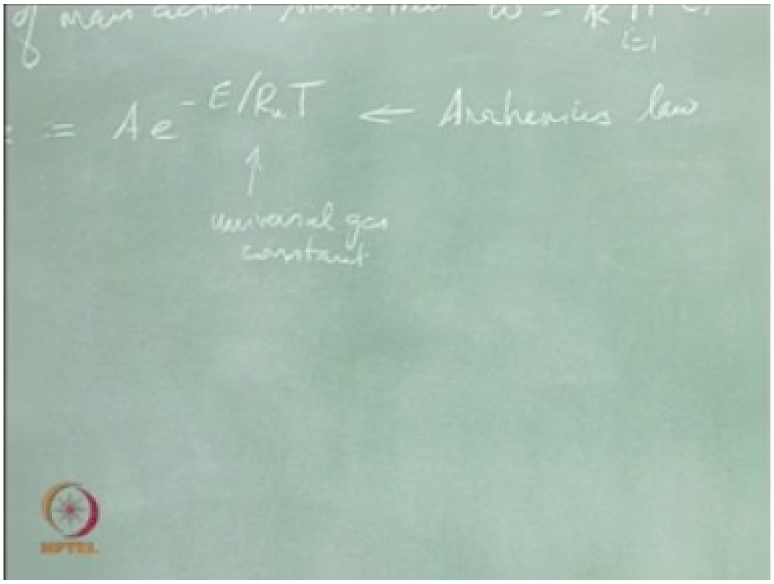

of mass action $\omega = K \prod_{i=1}$

$= Ae^{-E/R_uT}$ ← Arrhenius law

universal gas constant

K = Ae – e over R_UT or sometimes there is a subscript A to e here so to indicate its activation energy but it is essentially activation energy there, so e to the exponential e exponential to the negative u or U_T or U stands for universal gas constant, right in the or e so this is the this is what is called as the Arrhenius is law the Arrhenius law essentially gives you the temperature dependence of the rate constant well or this rate constant is also called specific reaction rate okay it is essentially the reaction rate for unity concentrations of the reactions the reactants.

So that is called specific reaction rate but it is also called the rate constant but it is not really a constant it depends on the temperature and the Arrhenius law essentially gives you the temperature dependence you can also write this, if you want to now include.

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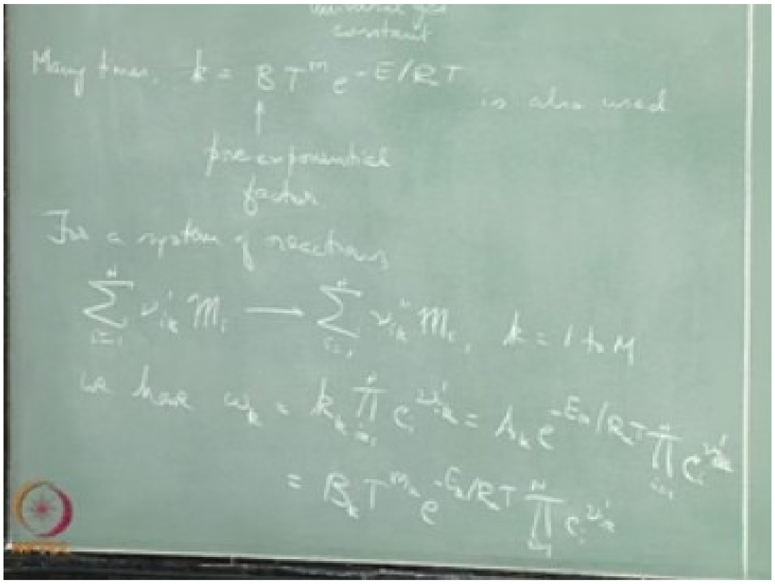

constant

Many times, $k = BT^m e^{-E/RT}$ is also used

pre exponential factor

For a system of reactions

$$\sum_{i=1}^{N} \nu'_{ik} M_i \longrightarrow \sum_{i=1}^{N} \nu''_{ik} M_i, \quad k = 1 \text{ to } M$$

we have $\omega_k = k_k \prod_{i=1}^{N} C_i^{\nu'_{ik}} = A_k e^{-E_k/RT} \prod_{i=1}^{N} C_i^{\nu'_{ik}}$

$= B_k T^{m_k} e^{-E_k/RT} \prod_{i=1}^{N} C_i^{\nu'_{ik}}$

Many times many times K = BT^m e to – e E/RT is also used that means there is a polynomial dependence of the rate constant on temperature that is T to the m and there is a exponential dependence on temperature okay, so the exponential dependence obviously is a lot stronger dependence when compared to the polynomial dependence so sometimes you could you could tend to ignore it and say let us not worry about the polynomial dependence that simply take Ae – E/RT right.

And the day there you are taking in only the exponential dependence the exponential dependence is the biggest problem with Commerce okay, so what we are actually now going through is in some sense like the is one of the biggest stumbling blocks in solving combustion problems the exponential dependence is a highly nonlinear dependence okay, so essentially this is what and depends depending upon the value of E and typically when the value of E is larger and larger the non-linearity the nonlinear dependence of K or the reaction rate in general on temperature becomes more.

Nonlinear okay so it becomes very, very sensitive to temperature that means it does not change over a fairly wide range of temperatures but you now cross a certain threshold temperature it just goes boom and what that means is, we should now be able to capture this variation within that very small change in temperature because the suddenly changed until then you do not have any reactions happen significantly speaking, right and all of a sudden you have all the reactions happening okay.

So there are very quick changes that keep happening in space or in time depending upon where you are looking at unsteady problems or both okay, so you typically also have a spatial very spatial resolution issue because of these things and this poses a what is called mathematically what is called as a stiff situation, so because when you are now looking at convection in a flow and then you have a flame and then suddenly when you go to the flame you are now having a sudden increase in temperature right.

And so long they are not being having such a high variation in temperature, so you are okay with resolving the temperature over larger distances and then suddenly we were here and where the flame is you know how to resolve very, very close and now begin to keep track of these fast changes in temperature, if you were to do the same thing over there it is sort of like there is hardly much change, so you are wasting your time doing that okay so for example if you do the computational methods.

You would want to take like a very coarse grid relatively speaking over there but when you get to the flame you want to now suddenly have a very fine grid, but you are supposed to find out what the flame is and therefore you should be you should adapt your grid and stuff it is difficult right, so typically you now have a much different length scale for combustion than for reactions so if in the same equation as we will see both the reactions and the convective processes occur and they are happening at two different length scales.

It is very difficult to resolve both of them for the grid with the same scale right and that is typically what is called as a mathematically stiff problem and you will get into these stiff problems primarily coming out of this yeah right, so we are just beginning to get into the gory details of combustion if you will yeah okay, so let me just box this for you to make it look good one of the things that I would like to say is whenever you are dealing with the Arrhenius law you are always using the universal gas constant never make a mistake never have any confusion about this okay.

So typically when you are busy writing an exam you are like they use the specific gas constant of the universal gas constant what do you do now no our genious always uses the universal gas constant okay, so this is something that you always keep in your mind when you are doing like back of the envelope calculations exam problems and so on, okay second point in this course we are now take going to take these as laws the means we are not going to ask how we got these okay how are you going to how did you get these did experiments hey.

I guess yeah so somebody actually took because poor things showed up and started measuring things is it out is that how did they figured yes that is true they did that okay you can also have a quantum-mechanical basis for this for example this is what is called as a A or B okay, so now we can call this pre exponential factor pre-exponential factor right, so from quantum mechanics we will be able to find out that this actually depends on probability of what is called as effective collisions okay.

So what is mean by effective collisions what it really means is you need to have molecules that collide actually come in at a particular orientation with respect to each other so it is like you have a molecule that means it has a bunch of atoms in a particular arrangement you have another molecule of atoms its atoms in a particular arrangement, when you now have a reaction that is going on it is one atom of this molecule and another atom of the other molecule that are the ones that are actually exchanging electrons.

And creating bonds there and then disrupting other bonds there right that means when they collide you need to have this particular atom of this molecule collide with that particular atom of that molecule that means they should or be oriented in particular ways right and the probability with which they would orient in those particular ways is less when compared to if you do not have to worry about the orientation right, so all that stuff is buried in the pre-exponential factor ok so you can derive these things from quantum mechanical basis and a good graduate course would do this right.

Or we would have a maybe we have another course like physical gas dynamics where you can actually go through all these things yeah, so that that is typically taught in the art semester that is like the ongoing semester, now so you can sit in a course there wherever you can learn all these things, but in this course we are now going to keep on adopting the continuum approach that means at a particular point you have a temperature that is defined you have a concentration that is defined and based on the concentrations the reaction rates are going to be determine and based on the temperature.

There the reaction rate constant is going to be determined by given by these laws in reality at every point in space where you have reactions happening you have like millions of molecules that are bombarding each other and going through reactions, we are not resolving that level of detail yes we do not want to define that in this course right, so one of the things that we go through in chemistry is something like a hill that you have to cross and then there is like a height of the hill that s activation energy.

We do not want to worry about all that stuff okay so because of this mathematically speaking you will also face a problem in thinking about ignition because, if this is your think about this if this is your K you now plug this in K and then you now get your ω right and plug the ω in here you get it ωi which is the rate of production of a particular species right, now let us suppose that we have a methane oxidation reaction that you are thinking about and let us do something very sinister right.

This something that I always do fill up this room with methane yeah and of course we have some oxygen otherwise, we would not be breathing here right what is going to happen are their reactions going on or not, I just filled up this room with a decent amount of meeting or the reactions going on auction is there right according to this yes right, so of course we have air conditioning and all those things, so the temperature here maybe like about 120^0 C right so you are looking at like little plug in R to 9 to 3 K over there right.

You will now get some value for different values of AE and so on and you plugged in plug it in there I will tell you what the concentration of them ethane is what the concentration of oxygen is plug it in there and then you know the reactions new I double Prime and you are single prime then you can find out the rate of production of carbon dioxide or rate of production of water or rate of product depletion of methane all these things right.

You will find some values which are nonzero what do you do the means you just fill in some methane and here reactions are going to go on hey that is dangerous what is happening I have not it ignited that means we do not have a flame that is propagating ,we are not burning yet right and we are still at 293 Kelvin 20^0C, so but there are reactions going on any not any idea of this number like what would be your ω that would be extremely low 10 to the - 14 - 15 that kind of thing for room temperatures okay.

So from a mathematical point of view what this actually means and we will relate this to what is called as a cold boundary difficulty okay, that means we really strictly speaking cannot identify reactants as completely reactants okay because even as they are just being reactants they strictly speaking in principle should be reacting and producing products at a very minuscule rate according to this right, it becomes numerically significant when the temperature rises past a value that is like related to you.

Or are or you okay that is what this means then you begin to have values that are significant the heat released it is significant it begins to hurt us okay, and then we get burnt okay so keep this in mind we are not going to worry about what he means to us except to point out that the value of it is going to dictate the non-linearity of the reaction rates temp dependence on temperature okay that is what we want to worry about as far as we are concerned okay typically when you have a full fetched reaction.

That is going on and you think that you have a flame there the reaction rates are very high so of the order of it could be even 10 to the 10 right, so you are now going from one end like 10 to the - 10 to 10 to the 10 so that is another thing, so as I told you we are not only having like a very narrow region over the steep price happens but the steep price happens over a huge range, so you have to capture this numerically you know that the values that is very difficult that sets the biggest problem as far as combustion is concerned the chemistry that is there is thrown in there the exponential dependence of the reaction rate on temperature is the biggest will in chemistry okay that that makes the whole problem highly nonlinear and very stiff.

So I guess I cannot emphasize enough about this but we will just move on and then we now say for a system of reactions for a system of reactions, so how do you write a system of reactions you now say σi = n μi k single prime mi gives σi = n μi k double prime am I k = 1M, so capital M indicates the number of reactions that you are going to have right in a scheme of reactions and each of those reactions then the Kth reaction will be identical to any of the single reactions that we have seen before okay except.

We now want to identify the stoichiometric coefficients will decay it reaction as well as the ith species, so we now say it has two subscripts new-new I case single trying a new double a new ik double prime these, now become like matrices okay so this then means that you are looking at a multi-step reactions reaction sequence why would you worry about a system of reactions or a multi-step chemistry the reason is as I told you some time back a species that is produced in one reaction could be consumed in another reaction.

So the net production that they did the net rate of production of or depletion of a species will now be dependent on what how much is produced in each of the chemical reactions right, so that is what we are going to keep track of so, so we have for free for a system of reactions notated by this we have ωK we, now have the common quantity reaction rate, now specific for the case reaction okay, so the kids reaction the reaction rate for the Kth reaction is equal to K_K πi = n ci u new ωi K single prime okay.

And that is equal to Ak_e to the – dk /RT πi =1 to ci K single prime right well if you want to do one walk $B_K T$ to the m_K e to the – e - ek πi = 1 to n ci to the new I k single prime, so they look at what is going on.

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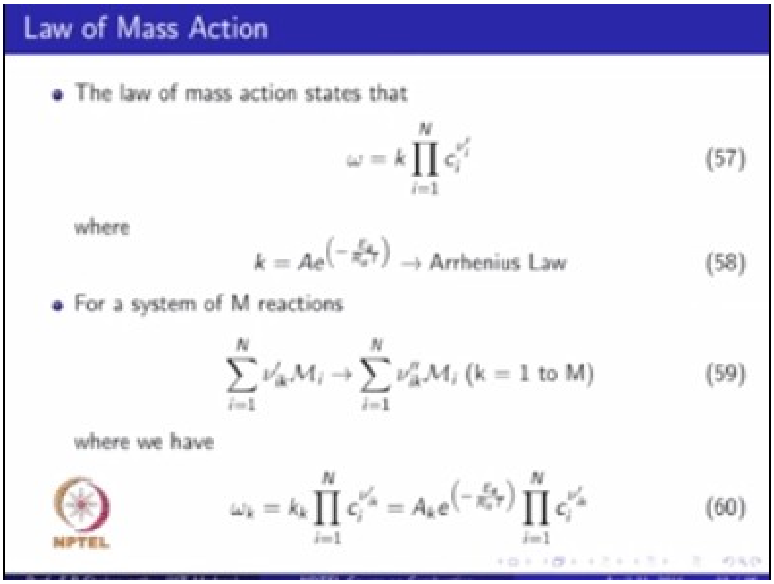

Law of Mass Action

- The law of mass action states that

$$\omega = k\prod_{i=1}^{N} c_i^{\nu'_i} \quad (57)$$

where

$$k = Ae^{\left(-\frac{E_a}{R_u T}\right)} \rightarrow \text{Arrhenius Law} \quad (58)$$

- For a system of M reactions

$$\sum_{i=1}^{N} \nu'_{ik}\mathcal{M}_i \rightarrow \sum_{i=1}^{N} \nu''_{ik}\mathcal{M}_i \ (\text{k} = 1 \text{ to M}) \quad (59)$$

where we have

$$\omega_k = k_k\prod_{i=1}^{N} c_i^{\nu'_{ik}} = A_k e^{\left(-\frac{E_k}{R_u T}\right)}\prod_{i=1}^{N} c_i^{\nu'_{ik}} \quad (60)$$

We are now having a sudden explosion of the number of parameters that we have to consider okay, so previously I said these are going to be given to us okay, so we now have a reaction you know what the new I single Prime and you I double Prime's are, so that was given to you so you are looking at what this was and that is given by this reaction that means we need to be supplied with these two values a and E okay if you now want to further take the polynomial dependence of temperature then you need to have be m and E okay.

So for a given reaction you need to be given be m and E these are what is called the kinetic parameters okay and the information on new I single prime a new I double prime is essentially giving you what the reaction is okay it is a N and what the script M is are the new I and knew I knew I single prime I knew I double prime is what is going to give you what the reaction is in the system of react reactions your N capital M µ the descript M is and the new I single Prime's new like a single primes the new iK that finds.

All this information gives you what is called as a reaction scheme the reaction scheme is nothing but a list of reactions okay, you only see the list of reactions you should be able to find out what is a capital n what is the total number of species, okay and I going from 1 to N what are the species script am I and how many reactions are there capital M okay, IK going from 1 to M what are the reactions that is given by that that will be identified by a new ice new like a single prime a new on K double prime but we should be able to deduce all those things given a scheme of reactions.

But that is only one part of the story that is only telling you what is the chemistry right the species took and reacted with this species to produce that species and that else and then some of those species reacted with this so you have a scheme then there is another part of the story so one thing is to actually figure out the chemistry and the other thing is to actually figure out B_K N_K + e_K for each of those K^{th} reactions.

These are the chemical kinetic parameters okay so chemical kinetic parameters many times are quite difficult to measure and obtain even, if you were to figure out the reaction scheme you see so what we are and then most of the time the combustion expert or the combustion scientist tries to from a chemistry person to get give this information, so you have to actually get this information from a chemistry person first of all find out about the chemistry is that mean what is the reaction scheme.

That will give you the new I single can you like a single prime you okay double prime script mi 4i go going from1 to capital and what is capital n and what is the M all these things that is only the scheme in addition to this we have to get B_K m_k + E_K these three parameters for each of the reactions that is a get many times you get into your chip problem there.

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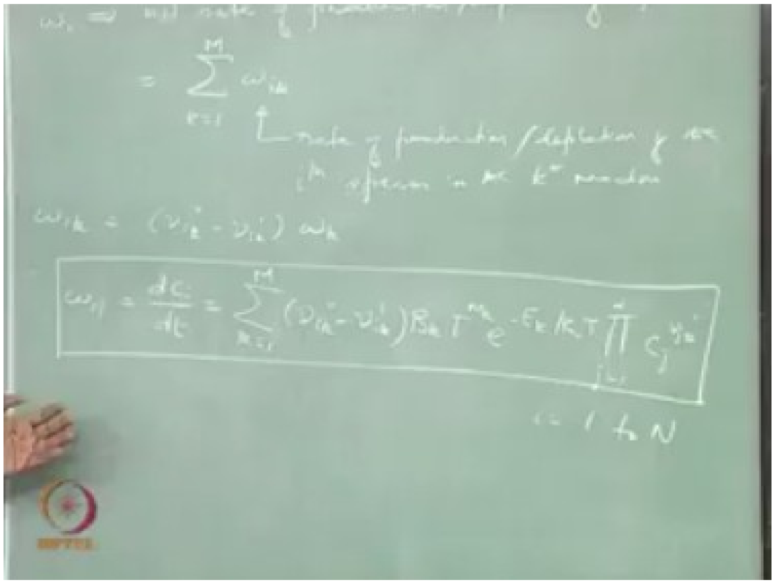

$\omega_i \Rightarrow$ net rate of

$$= \sum_{k=1}^{M} \omega_{ik}$$

rate of production/depletion of the i^{th} species in the k^{th} reaction

$$\omega_{ik} = (\nu''_{ik} - \nu'_{ik})\,\omega_k$$

$$\boxed{\omega_i = \frac{dc_i}{dt} = \sum_{k=1}^{M} (\nu''_{ik} - \nu'_{ik}) B_k T^{\alpha_k} e^{-E_k/kT} \prod_{j=1}^{n} c_j^{\nu'_{jk}}}$$

$i = 1$ to N

So here just to record whatever I am saying this the specific reaction grade of kth reaction and right now ω I remains the same as what we had before right ω I is the net rate of production or depletion of species I net rate of production or depletion of species I this will be equal to σ K equals 1to capital M ωik so where ωiK is rate of production or depletion of the ith species in the kth reaction that means in eve every reaction you have some for a rate of production or depletion of each species right.

That is ωik you sum over all the reactions to find out so in one reaction ωik could be positive another reaction ω it could be negative if it is negative that means it is depleting there as positive it is being produced you know add up all the stuff algebraically right you should, now get the net rate of production of that particular species and that is what we will care about the reason we will care about that is because just like how we normally do a mass conservation okay, in your fluid mechanics in addition to doing mass conservation for the mixture of species.

We will also now do a mass conservation for every species and obviously each of the species mass does not remain constant, so to conserve does not means it is going to be a constant okay what it means is whatever is the rate of change of mass will be equal to the net rate of production or depletion that is what that is what we will do as we go along, so we will factor this in into the mass conservation equation of individual species as a next step, so this is going to be very important to us.

Yeah so ωikn = μik double prime – μik single prime μk that is like the multi step version of this over here right, we did this money for one reaction, we now do this for decay its reaction and a multi reaction step, now we have to plug this back in here ad over all the reactions to get the net rate of production of a particular species right, so therefore ωi = to this is nothing but dci /dt that remains the same there you see ω is dci/dt right, so dci over dt that is equal to σk equals one to M μik double prime – μik.

Single prime K and ωk is B_KT to the MK e id exponential - e ek /RTπ J = 1 to n I am just using a different running variable just to avoid confusion CJ to the new JK single prime right.

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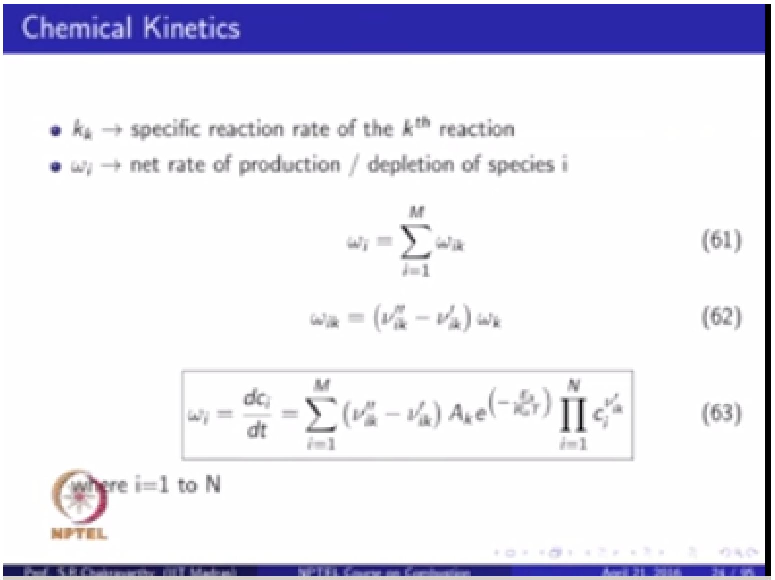

Chemical Kinetics

- $k_k \rightarrow$ specific reaction rate of the k^{th} reaction
- $\omega_i \rightarrow$ net rate of production / depletion of species i

$$\omega_i = \sum_{i=1}^{M} \omega_{ik} \qquad (61)$$

$$\omega_{ik} = \left(\nu''_{ik} - \nu'_{ik}\right) \omega_k \qquad (62)$$

$$\boxed{\omega_i = \frac{dc_i}{dt} = \sum_{i=1}^{M} \left(\nu''_{ik} - \nu'_{ik}\right) A_k e^{\left(-\frac{E_k}{R_u T}\right)} \prod_{i=1}^{N} c_i^{\nu'_{ik}}} \qquad (63)$$

where i=1 to N

What do we have here what do we have here you, now say dci over dt is equal to a lot of things all now put together, so we just started learning something and then pretty soon we now have a all of them collapse together right in one line and finally you know have a dci over dt going all the way you have a πJ equals1 to n c CJ to the U_J K single Prime okay which means this contains the product of all the species which are reactants right in the KS reaction and you now sum over all the K reactions.

So pretty much all species concentrations are now going to figure in here right as product in one term and then you are going to have many of those terms added up for each of the reactions right so you will now have dci over dt for ith species equal to one term plus another term plus another term and so on each of those terms is for each each reaction and each term contains products of species concentrations possibly of the same species for which we wrote the dci by dt so two things are emerging here one the rate of change of concentration of species I depends on the concentrations.

Of all species practically or in general that means you cannot evaluate the constant rate of rate of change of concentration of species I independent of all other species you have to know the concentrations of all species to be able to find out what is rate of change of this right this means you now have for this box you should be able to write I equals 1 to n that means this is actually n reactions for each species, so n equations for each species right and all these equations are simultaneous set of equations they are all coupled to each other.

Because the rate of change of this is B going to depend on all other concentrations to find out the rate of change of so if you want to find out CI you now do a time integration of this right, so if I were to give the concentrations that are initially present for a set of reactions right from there I should now be able to do a time integration, so now integrate this in time to go to the next step night time next time okay.

During this time lot of species would have got consumed a lot of species would have got produced all those things are actually present over here that means I have to solve the next to dc by dt for the next species and, soon so all of them should be solved simultaneously so it is a simultaneous set of first order ordinary differential equations which we have to integrate in time simultaneously for all of them right this is the this is only the starting they are only scratching the surface.

Here now look at the nature of these equations the nature of the equations is first of all these are highly nonlinear not because of the huge and that I made about the temperature dependence that is the non-linearity in the temperature dependence that is showing up here, okay in each of these terms that is bad enough that that is something that I will come to next okay the non-linearity is because you now have each of these see Is is and unknown you are solved for simultaneously and these unknowns are actually showing up as products right.

So anytime you have products of unknowns you have nonlinear equations right and not only that even if they did not show up as products they are raised to possibly a non-unity exponent right, so anytime you have like a square or cube or - 0.1 anything other than one is nonlinear okay, so linear is only one thing it is like 1 okay nonlinear means anything else right that is going to screw up your day and making make it nonlinear right so you already have a nonlinear set of first order of these.

Here and then on top of this we will have to find out in reality in real combustion applications we would not know what the temperature is ok and the temperature keeps changing from place to place or time to time or both place in time the means we have to now have another equation that governs temperature and that equation also will be coupled with this equation because in order to solve that equation you needed to know what was the heat that was produced by these reactions to change the temperature and we will see that as we go along and in order for you to solve this know.

This is all this equation you need to know the temperature so in addition to this n equations that are getting couple you will also have an energy equation that gets coupled with this okay because the temperature is coupled to the species and the species a couple to the temperature, but if you are given temperature it is possible for you to today let us say you are now taking like about that has now maintained at a particular temperature and you wanted to know what should be the concentration of species that are produced given an initial set of species.

This is this is an initial value problem because it is a or EE in time right that means you can integrate in time given initial conditions for the concentrations of the species you should not be able to advance in time so if given temperature the energy equation gets decoupled from this set of equations but in a real practical problem you will have both of them coupled and this becomes a nasty set of equations as is without even worrying about convection and diffusion of species yet so we are now beginning to begin to look a look at combustion like right it just becomes gory and gory by the minute from here on see you tomorrow you.

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