Turbulent Combustion: Theory and Modelling
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Lecture – 7
Thermo -Chemistry (Contd.,) and Chemical Kinetics

Welcome back, let us continue the discussion on combustion on thermo chemistry. So we are almost looking at different things of thermochemistry. So that gives you an idea about fundamentals of basic combustion.

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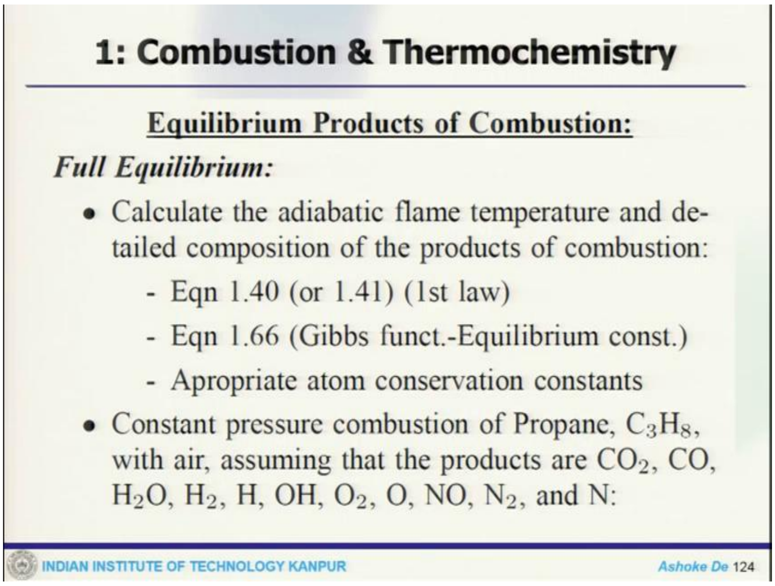

1: Combustion & Thermochemistry

Equilibrium Products of Combustion:

Full Equilibrium:

- Calculate the adiabatic flame temperature and detailed composition of the products of combustion:
  - Eqn 1.40 (or 1.41) (1st law)
  - Eqn 1.66 (Gibbs funct.-Equilibrium const.)
  - Apropriate atom conservation constants
- Constant pressure combustion of Propane, C_3H_8, with air, assuming that the products are CO_2, CO, H_2O, H_2, H, OH, O_2, O, NO, N_2, and N:

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So, where do you stop actually now looking at the Gibbs function and all these things? We will continue from there and let us discuss two other things under this thermochemistry, and then we will move to the next discussion on kinetics. Now equilibrium product that is one important thing when the reaction takes place, for example, you taken the reaction on methane with air say oxygen to give you CO_2 + H_2O now, when the combustion takes place completely in the sense the there is no excess oxygen or there is no access methane.

Then there will be product which will be formed in the time, some major species likes CO_2 and H_2O for example, this reaction is not a complete one. Then you might get some extra component like CO, O_2 something like that. Those are the some of the intermediate component that may remain in the combustion product actually, everything is complete and you can calculate the same temperature and which we have already discussed. And these are all the detail readout in these previous equations covered in the lecture. Now you have a constant pressure combustion of propane $C3H_8$ with air that means it will be a combination of oxygen and nitrogen assuming that the products are CO_2, CO and this thing.

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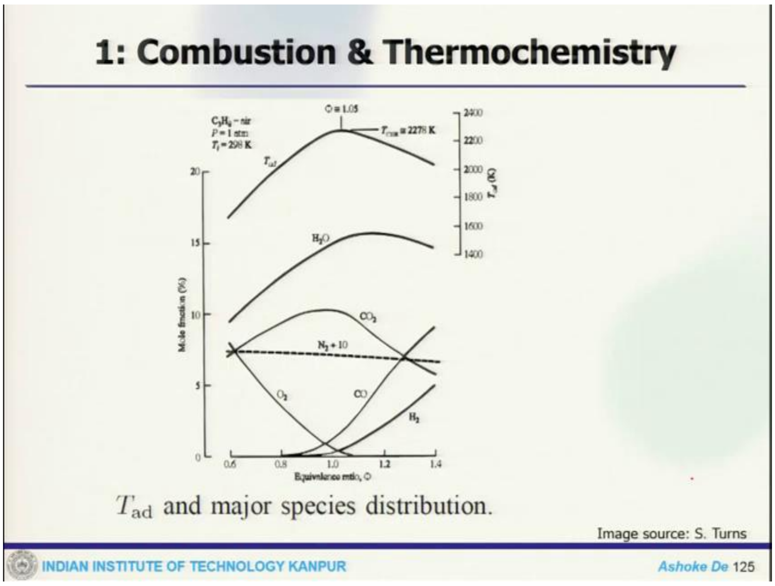

1: Combustion & Thermochemistry

T_{ad} and major species distribution.

Image source: S. Turns

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So the adiabatic flame temperature is under the major species distribution and what you can see here is that in the x-axis you have an equivalent ratio and this is mole fraction and the temperature here is the adiabatic flame temperature. This is adiabatic flame temperature. So this bar is along the equivalent ratio and close to 1 which is sort of approximately 1 is that stoichiometric condition. And that means in the stoichiometric condition everything is; so neither fuel rich nor fuel lean; so it is complete combustion which one would expect and the temperature rises the maximum.

So, you can see in the temperature variation it is going up because once you increase the fuel that means you increase the equivalent ratio, temperature is going up but it reaches maximum and then again falls down because φ greater than one it is a condition which will lead to the deterioration of that temperature. Now other factor is the mole factor when you look at the mole fraction some stable products are there one is that O_2 will be consumed like this.

Then you have CO formation, H_2O formation, CO_2 formation these are the some of the distribution looks like in that fashion.

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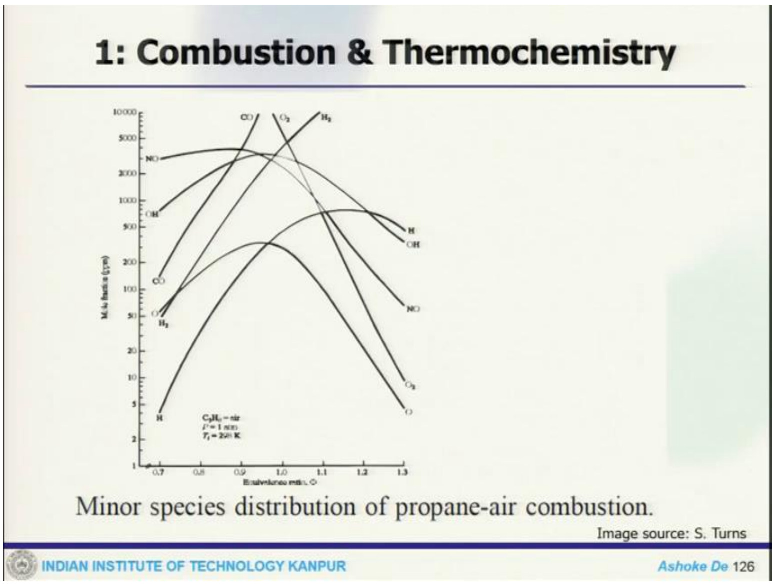

1: Combustion & Thermochemistry

Minor species distribution of propane-air combustion.

Image source: S. Turns

Now one may also would be interested to look up the distribution of minor species and a minor species are like CO, OH are different kind of radicals CO, OH, O, NO, H these are all radicals are minor species which one can actually look at the distribution along with the φ and then see their distribution also, but this is very specific propane combustion C_3H_8.The combustion is different or the fuel is different the distribution is high. This is a representative figure shows you how the major and minor species for varying equivalence ratio.

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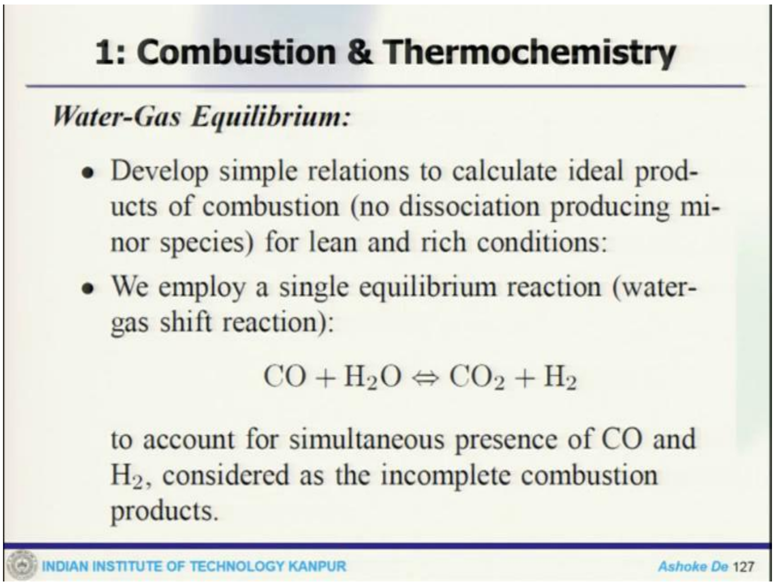

1: Combustion & Thermochemistry

Water-Gas Equilibrium:

- Develop simple relations to calculate ideal products of combustion (no dissociation producing minor species) for lean and rich conditions:
- We employ a single equilibrium reaction (water-gas shift reaction):

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

to account for simultaneous presence of CO and H_2, considered as the incomplete combustion products.

Now another part of it is the water gas equilibrium. That means so you need to get some kind of an idea when there is water remain in vapour form some liquid form in the combustion. So, you can actually find out from a single equilibrium reaction like when CO is reacting with H_2O, you form CO_2 and H_2O. Now to account for simultaneous presence of CO and H_2, you consider this product and then you can calculate it.

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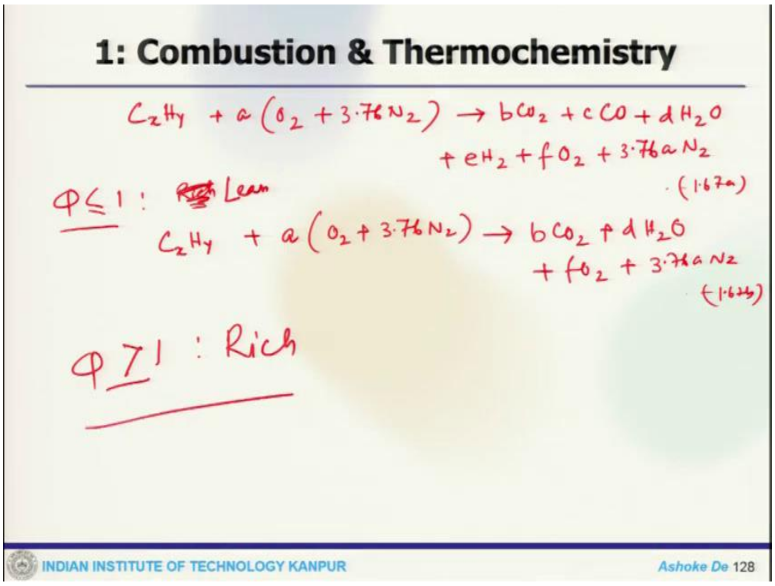

1: Combustion & Thermochemistry

$$C_zH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2 \quad \cdot (1.67a)$$

$\varphi \leq 1$: Lean

$$C_zH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + dH_2O + fO_2 + 3.76aN_2 \quad \cdot (1.67b)$$

$\varphi > 1$: Rich

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So, any hereditary hydrocarbon if you consider let us say C_zH_y and it bonds with air. You get this is air times then you get CO_2, CO, H_2O, H_2, O_2 and 3.76 a multiply by N_2. Now for condition φ less than equal to 1, if you have a condition like that, then your $[C_xH_y + a(O_2 + 3.76N_2)]$, this will only become $[bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2]$. So, that is what you get so this is your fuel rich condition, another condition which could be possible is the fuel lean condition.

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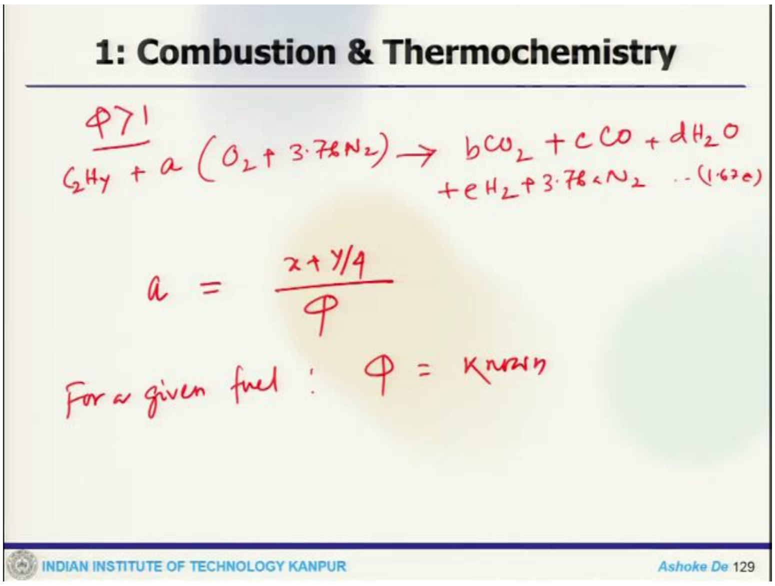

1: Combustion & Thermochemistry

$\varphi > 1$

$$C_zH_y + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + 3.76aN_2 \quad \cdot\cdot (1.67c)$$

$$a = \frac{x + y/4}{\varphi}$$

For a given fuel : φ = Known

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So, when this fuel rich condition that means for φ greater than 1, you expect the fuel is more; so you do not have any product and fuel will be there because fuel is more, so they are not sufficient to bond that intermediate carbon and you get H_2O plus hydrogen and nitrogen. So, depending on your condition whether rich or lean you get the different kind of product that will come. Now fuel can be correlated with φ like:

$$a = \frac{x + {}^{y}/_{4}}{\varphi}$$

So, for a given fuel, φ is known. Then one can find out rest of the quantities.

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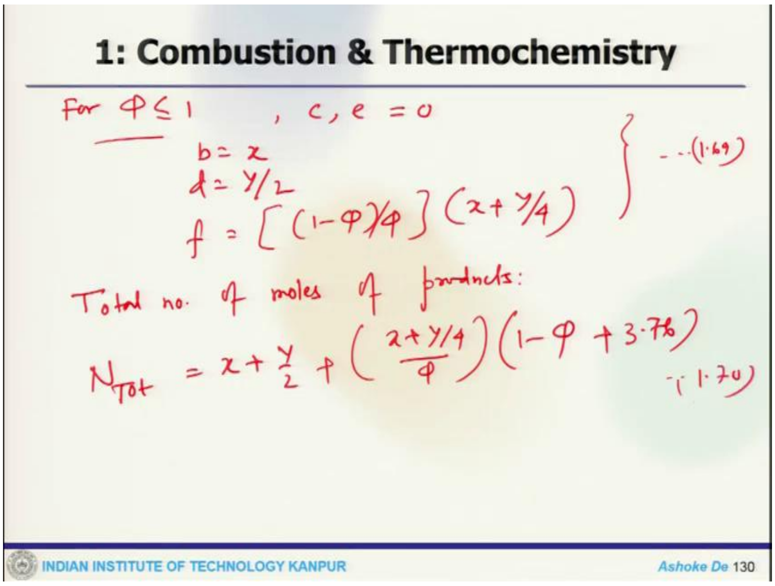

1: Combustion & Thermochemistry

For $\varphi \leq 1$, c, e = 0

$$\left.\begin{aligned} b &= x \\ d &= y/2 \\ f &= [(1-\varphi)/\varphi](x + y/4) \end{aligned}\right\} \quad \text{---(1.69)}$$

Total no. of moles of products:

$$N_{Tot} = x + \frac{y}{2} + \left(\frac{x + y/4}{\varphi}\right)(1 - \varphi + 3.76) \quad \text{-(1.70)}$$

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Now we can do that calculation for condition φ less than 1 where c, e they would be all zero. b becomes x and d becomes (y/2), f becomes:

$$f = \left[{}^{(1-\varphi)}/_{\varphi}\right]\left(x + {}^{y}/_{4}\right)$$

So that is essentially the equation 1.69. So, total number of moles of products N_{total} is:

$$N_{tot} = x + \frac{y}{2} + \left(\frac{x + {}^{y}/_{4}}{\varphi}\right)(1 - \varphi + 3.76)$$

So that is my total information.

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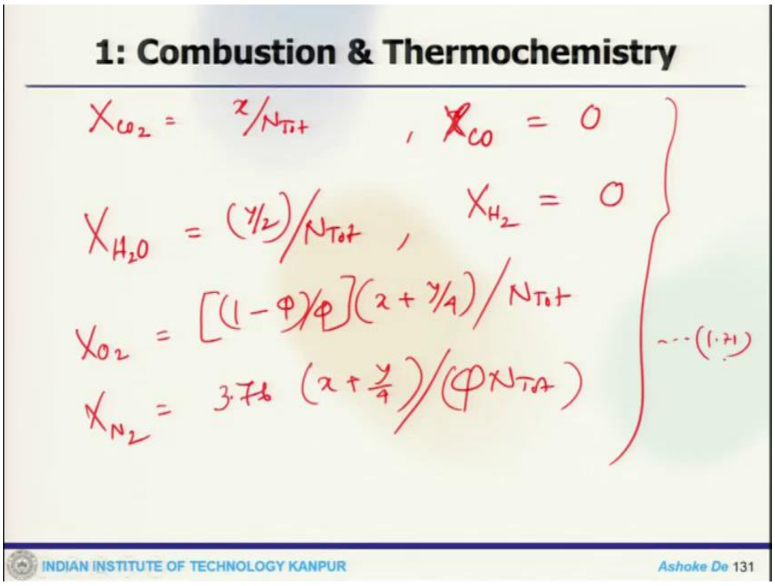

1: Combustion & Thermochemistry

$$\left.\begin{aligned} X_{CO_2} &= x/N_{Tot}, \quad X_{CO} = 0 \\ X_{H_2O} &= (y/2)/N_{Tot}, \quad X_{H_2} = 0 \\ X_{O_2} &= [(1-\varphi)/\varphi](x + y/4)/N_{Tot} \\ X_{N_2} &= 3.76\,(x + \tfrac{y}{4})/(\varphi N_{Tot}) \end{aligned}\right\} \text{---}(1.71)$$

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So, we can further calculate the mole fraction that means for X_{CO_2} would be:

$$X_{CO_2} = {}^{x}\!/_{N_{tot}}$$

where X_{CO} is zero, X_{H_2O} would be:

$$X_{H_2O} = {}^{({}^{y}\!/_{2})}\!/_{N_{tot}}$$

$X_{H_2}$is zero, X_{O_2} is:

$$X_{O_2} = \left[{}^{(1-\varphi)}\!/_{\varphi}\right] {}^{(x + {}^{y}\!/_{4})}\!/_{N_{tot}}$$

And $X_{N_2}$is:

$$X_{N_2} = 3.76\, {}^{(x + {}^{y}\!/_{4})}\!/_{(\varphi N_{tot})}$$

So these are the all mole fraction that one can get.

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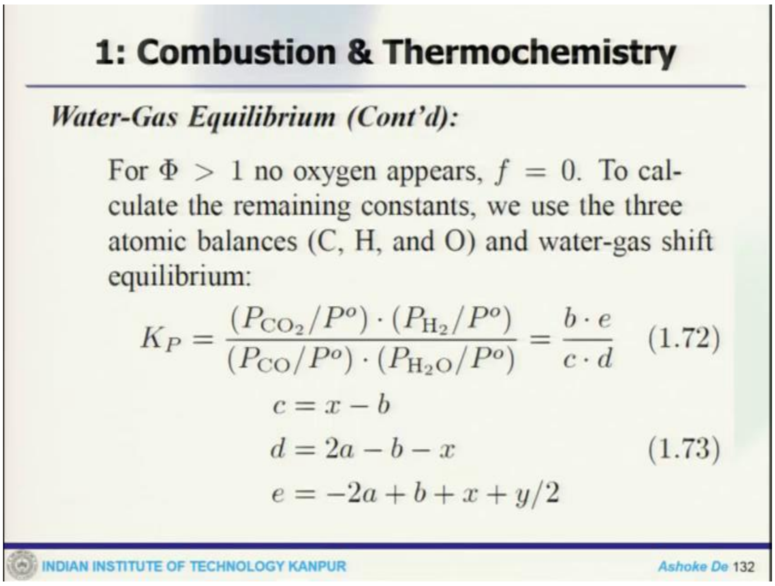

1: Combustion & Thermochemistry

Water-Gas Equilibrium (Cont'd):

For $\Phi > 1$ no oxygen appears, $f = 0$. To calculate the remaining constants, we use the three atomic balances (C, H, and O) and water-gas shift equilibrium:

$$K_P = \frac{(P_{\mathrm{CO_2}}/P^o)\cdot(P_{\mathrm{H_2}}/P^o)}{(P_{\mathrm{CO}}/P^o)\cdot(P_{\mathrm{H_2O}}/P^o)} = \frac{b\cdot e}{c\cdot d} \quad (1.72)$$

$$\begin{aligned} c &= x - b \\ d &= 2a - b - x \quad (1.73) \\ e &= -2a + b + x + y/2 \end{aligned}$$

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Now if you have φ >1 that means fuel in rich condition so you have no oxygen which will appear that means air would be zero. So to calculate the remaining constant you can use the three atomic balances for C, H and O water gas shift equilibrium. So, where K_p is:

$$K_p = \frac{\left({P_{CO_2}}/{P^0}\right)\left({P_{H_2}}/{P^0}\right)}{\left({P_{CO}}/{P^0}\right)\left({P_{H_2O}}/{P^0}\right)} = \frac{b.e}{c.d}$$

This already we have derived the equilibrium constant and from there one can find out C would be (x – b), d would be (2a – b - x) one can find out on his own and find out these coefficients.

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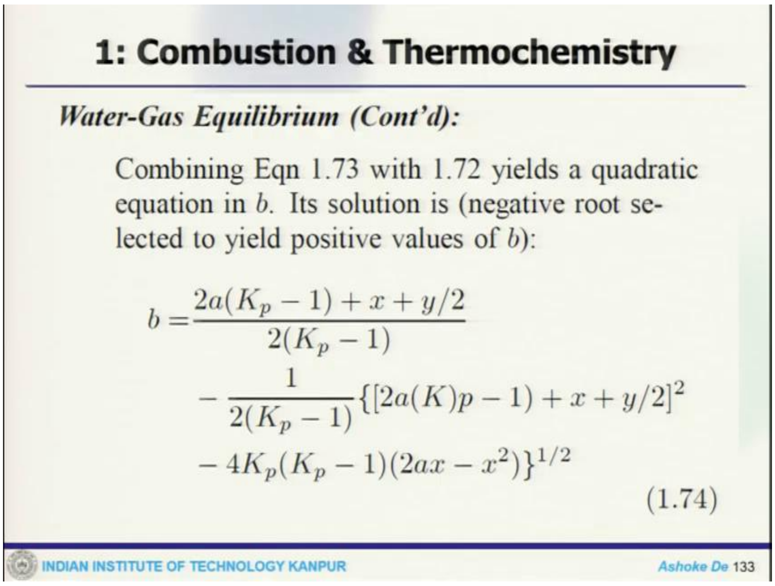

1: Combustion & Thermochemistry

Water-Gas Equilibrium (Cont'd):

Combining Eqn 1.73 with 1.72 yields a quadratic equation in b. Its solution is (negative root selected to yield positive values of b):

$$\begin{aligned} b = &\frac{2a(K_p - 1) + x + y/2}{2(K_p - 1)} \\ &- \frac{1}{2(K_p - 1)}\{[2a(K)p - 1) + x + y/2]^2 \\ &- 4K_p(K_p - 1)(2ax - x^2)\}^{1/2} \end{aligned} \quad (1.74)$$

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Now, once you combine this equation 1.73 that is this one and this one you get an quadratic equation in b and the solution is kind of you will get; this is the equation that so is nothing but putting back all this information in this and you get this quadratic equation.

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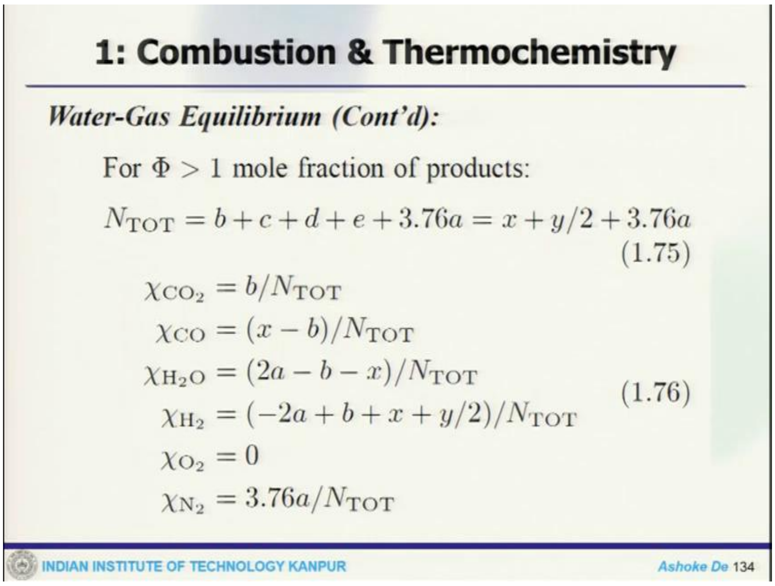

1: Combustion & Thermochemistry

Water-Gas Equilibrium (Cont'd):

For $\Phi > 1$ mole fraction of products:

$$N_{\mathrm{TOT}} = b + c + d + e + 3.76a = x + y/2 + 3.76a \qquad (1.75)$$

$$\begin{aligned} \chi_{\mathrm{CO_2}} &= b/N_{\mathrm{TOT}} \\ \chi_{\mathrm{CO}} &= (x-b)/N_{\mathrm{TOT}} \\ \chi_{\mathrm{H_2O}} &= (2a-b-x)/N_{\mathrm{TOT}} \\ \chi_{\mathrm{H_2}} &= (-2a+b+x+y/2)/N_{\mathrm{TOT}} \\ \chi_{\mathrm{O_2}} &= 0 \\ \chi_{\mathrm{N_2}} &= 3.76a/N_{\mathrm{TOT}} \end{aligned} \qquad (1.76)$$

So, you get $\varphi > 1$ mole fraction for the product, you can estimate the total mole fraction and then rest of the mole fraction for individual element. So, you have CO_2 you get CO you get H_2O and then H_2, O_2 will be zero and this. This is how one can estimate actually all these things basically the equilibrium products and all these things. So, that would essentially give you an idea about your thermochemistry.

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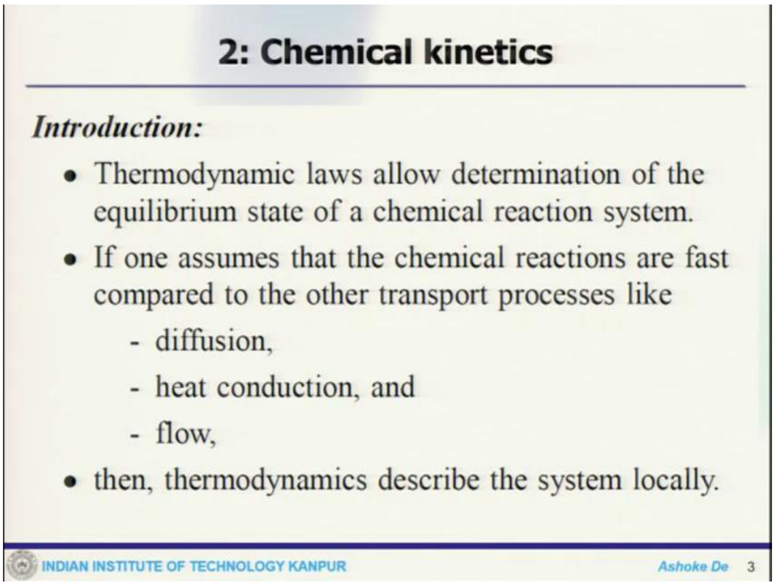

2: Chemical kinetics

Introduction:

- Thermodynamic laws allow determination of the equilibrium state of a chemical reaction system.
- If one assumes that the chemical reactions are fast compared to the other transport processes like
  - diffusion,
  - heat conduction, and
  - flow,
- then, thermodynamics describe the system locally.

And now we will go to the kinetic because one of the important things that is required to understand is the Kinetics because Kinetics is going to play an important role when you talk about all this reaction system and all this things that every action system and what we are looking so far is the Global kinetics like CH_4 or C_3H_3 hydrocarbon, when it is reacting with the air or oxygen you get to see.

But in reality, the reaction actually goes to multiple state. So, that is what now we are going to look at now the kinetics part and the kinetics part the wave, we want to see how this individual reaction steps. And so that will allow you to determine the equilibrium state chemical reactions and everything. So now if you assume that the chemical reaction are fast and compared to the other transport processes then like the transport process like one of the important process is diffusion.

So when there are multiple species which are actually interactive in a system, actually there is diffusion takes place which is an important, then you have flow field conduction. So you can see this thing.

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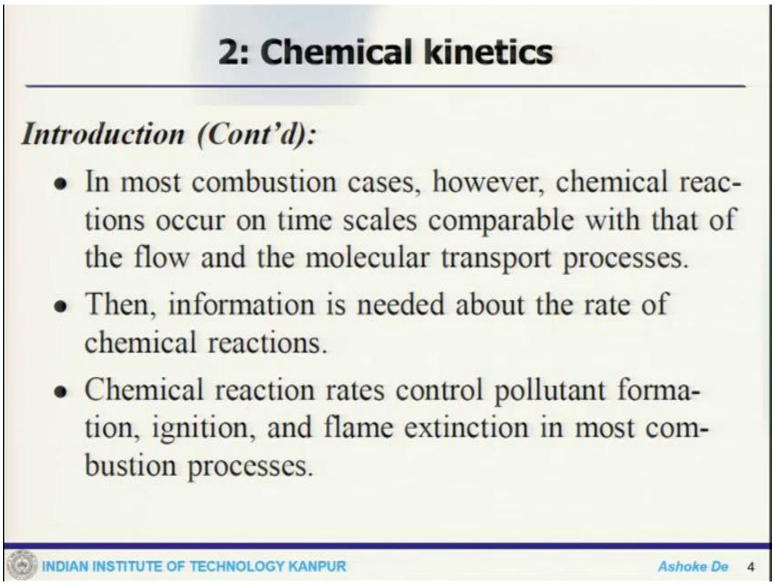

2: Chemical kinetics

Introduction (Cont'd):

- In most combustion cases, however, chemical reactions occur on time scales comparable with that of the flow and the molecular transport processes.
- Then, information is needed about the rate of chemical reactions.
- Chemical reaction rates control pollutant formation, ignition, and flame extinction in most combustion processes.

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Now most of the combustion cases so the chemical reaction time scale which is comparable with that of the flow and the molecular transport processes if they are comparable, but certain cases they are not when especially deal with the turbulent cases. So one need to know or have an idea about the rate of chemical reaction or the rather tou chem which is your chemical time scale one has to know that, that is what would be the time scale that one can get from the;

So, reaction rate controlled also this Kinetic they will control your pollutant formation. Ignition, remix.

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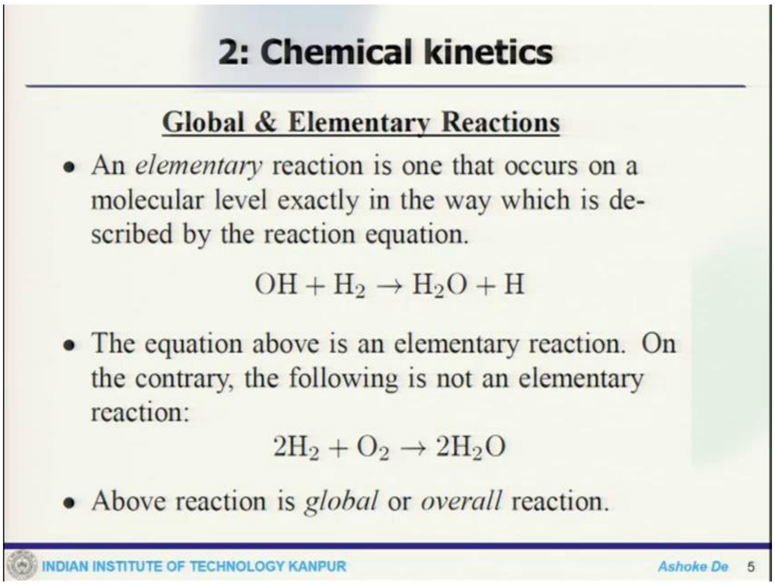

2: Chemical kinetics

Global & Elementary Reactions

- An *elementary* reaction is one that occurs on a molecular level exactly in the way which is described by the reaction equation.

$$OH + H_2 \rightarrow H_2O + H$$

- The equation above is an elementary reaction. On the contrary, the following is not an elementary reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Above reaction is *global* or *overall* reaction.

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These are the some of the important that you will have during the chemical reaction now, how you define; I mean so far away looking at the single step global kinetics now what we are now going to look at this now how this single step individual kinetics like for example it talk about methane combustion all the time with the air. So that goes to CO_2 and H_2O and if there is nitrogen, now this Global kinetics is something which is representative of the methane reaction but in reality this goes to multiple elementary steps. Now, so important things to know about this elementary reaction, so that actually occurs in all this process in reality.

So, now once you look at this elementary reaction example, you did reaction with you described by OH with hydrogen which will form H_2O and H, so this an elementary reaction so that means this is a part of a global reaction kinetics of hydrogen combustion. So there if you look at hydrogen with oxygen that will form H_2O this could be a global reaction where somewhere you get to see this kind of elementary reaction. Now the following is not as I said, this H_2 O_2, this is a global reaction.

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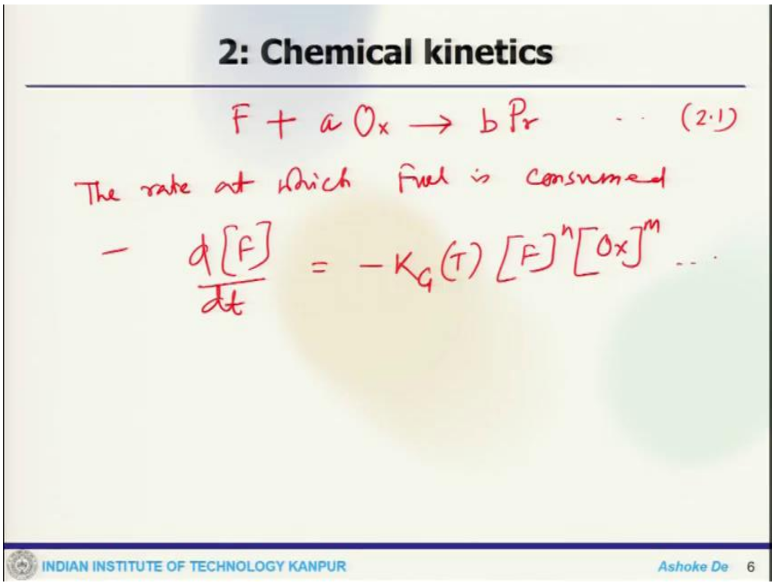

2: Chemical kinetics

$$F + a\,O_x \rightarrow b\,P_r \quad \cdots \quad (2.1)$$

The rate at which Fuel is consumed

$$-\frac{d[F]}{dt} = -K_G(T)\,[F]^n[Ox]^m \quad \cdots$$

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So, on one hand, we look at the global reaction and on the other hand you look at the; so now let us generalise the thing for a generic system, you have a fuel which is reacting with let say O amount of oxidizer to produce b amount of product. So, that is more genetic expression so we are not talking about any particular fuel or something or very specific fuel and the oxidizer. So, what experimental people have observed that the rate at which fuel is consumed that means the consumption rate. So that would the concentration change with respect to time it should be:

$$-\frac{d[F]}{dt} = -K_G(T)[F]^n[Ox]^m$$

So, that is what you get from this thing where X denotes the molar concentration of X.

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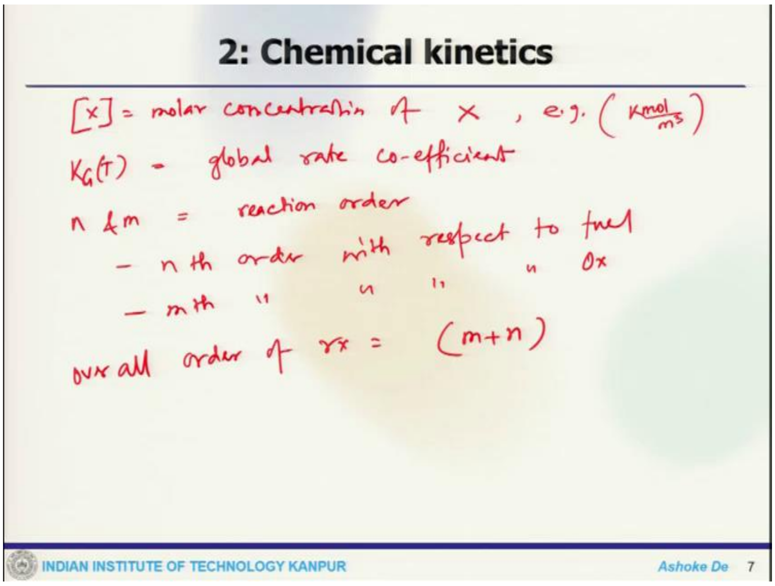

2: Chemical kinetics

$[x]$ = molar concentration of x, e.g. $\left(\frac{kmol}{m^3}\right)$

$K_G(T)$ - global rate co-efficient

n & m = reaction order

- n th order with respect to fuel
- m th " " " Ox

over all order of rx = $(m+n)$

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So, that means this is nothing but the molar concentration of X and if you look at the unit, it would be kilo Mole per metre cube. Where KG(T) is the global rate coefficient ok, where n and m these are the essentially they are related to the reaction order. Now, if you look at 2.2, as per 2.2, it is n^{th} order with respect to fuel but if you look at this is m^{th} order with respect to oxidizer. So, the equations say this is the consumption rate and should be F to the power n oxidiser to the power m so n^{th} order or m^{th} order.

And overall order of reaction is (m + n) now I mean m and n how can you determine that. So these are primarily determined from the experimental observation. And they do not be always integer. So there is one important thing to use in global reaction to express the chemistry. It is usually black box approach and has limited used in combustion because most of the realistic combustion are going to the detailed process.

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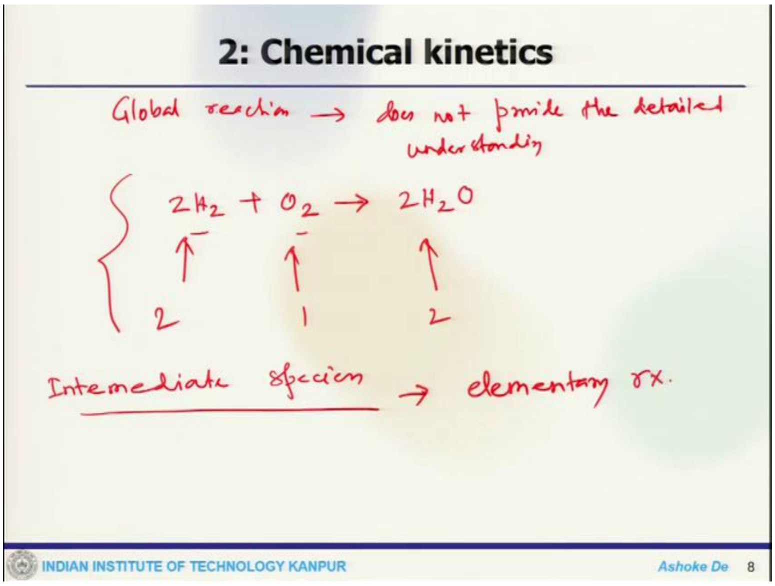

2: Chemical kinetics

Global reaction → does not provide the detailed understanding

$$2H_2 + O_2 \rightarrow 2H_2O$$

$\uparrow$ 2 $\quad$ $\uparrow$ 1 $\quad$ $\uparrow$ 2

Intermediate species → elementary rx.

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So, your Global reaction does not provide it does not provide the detailed understanding. So what is actually happening so let us takes an example, we can see that this is an global reaction for hydrogen-oxygen where hydrogen molecule react with oxygen to form 2 H_2O, so it implies 2 moles here, 1 mole here produce 2 moles of H_2O which is not strictly always true. In reality that could be something different because this is a global system, but there are lot of intermediate species which will form file this Global reaction is taking place.

So, this intermediate species are important and that is why one has to look at the elementary reactions for intermediate reaction, elementary reaction steps.

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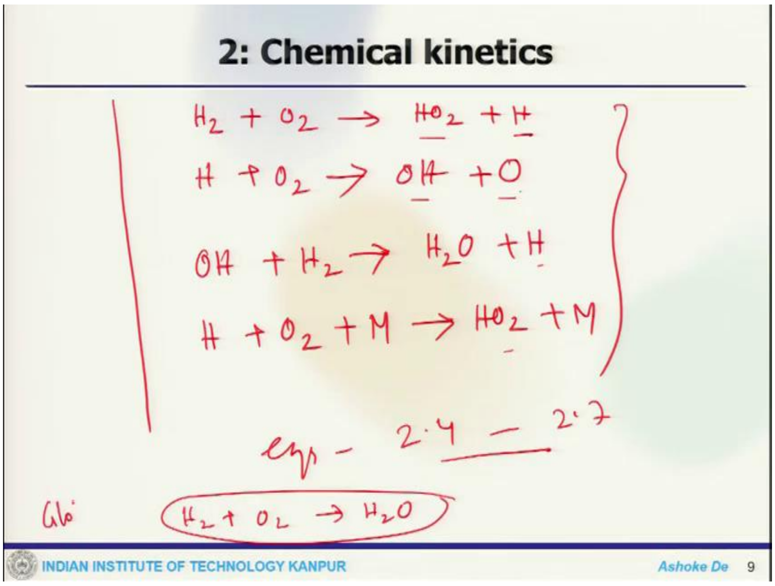

2: Chemical kinetics

$H_2 + O_2 \rightarrow HO_2 + H$

$H + O_2 \rightarrow OH + O$

$OH + H_2 \rightarrow H_2O + H$

$H + O_2 + M \rightarrow HO_2 + M$

exp - 2.4 — 2.7

Glo $\boxed{H_2 + O_2 \rightarrow H_2O}$

So, if you look at it, then there would be multiple elementary reaction like H_2 + O_2 can go to HO_2 + H, H + O_2 will form OH + O, OH + H_2 can form H_2O + H, H + O_2 + M from HO_2 + M so this are your equations 2.4 to 2.7 so these are the different elementary reaction where you can see there is H, HO_2, O, OH and another forms and final you get HO_2 and all these things.

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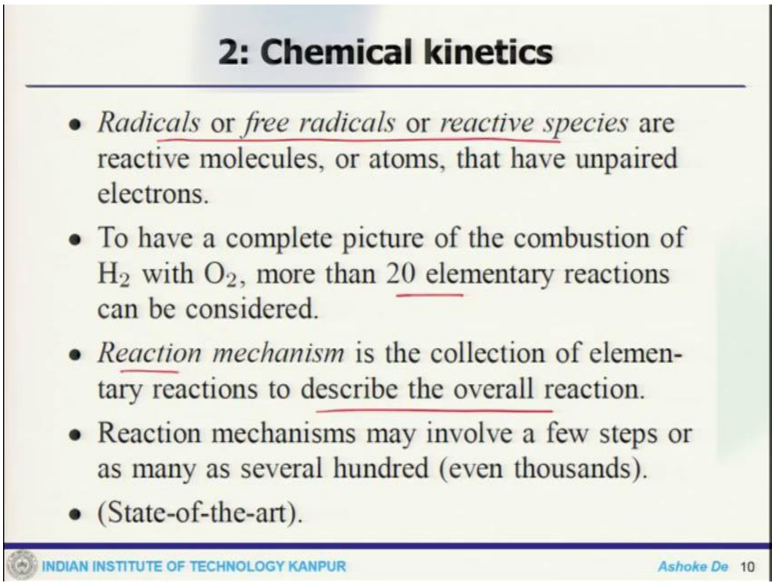

2: Chemical kinetics

- *Radicals* or *free radicals* or *reactive species* are reactive molecules, or atoms, that have unpaired electrons.
- To have a complete picture of the combustion of H_2 with O_2, more than 20 elementary reactions can be considered.
- *Reaction mechanism* is the collection of elementary reactions to describe the overall reaction.
- Reaction mechanisms may involve a few steps or as many as several hundred (even thousands).
- (State-of-the-art).

So, when you talk about all this thing that is this intermediate species are radical are called the free radicals or reactive species. So, that means the intermediate radical like what you have seen HO these are radicals, OH these are free radicals rather they are more reactive and they have unpaired electrons. And these radicals are actually quite important because these are the free radicals which allowed this reaction to propagate.

So actually to have a complete picture of the combination of this H_2 and O_2. More than 20 element reactions can be considered now, this is not always true that the only hydrogen and oxygen reaction can be defined with only one set of reaction kinetics. There could be multiple because there are different mechanisms. So the reaction mechanism for you call it is that when you look at this elementary step for global $H_2 + O_2$ to H_2O this is a global reaction.

So, these elementary reactions in set of these things are called the reaction mechanism. So that is essentially required to define, what describe the overall reaction that means is single hydrogen oxygen reaction can go through multiple elementary steps and those elementary steps one has to consider. This is true pretty much true for every fuel that in reality we have which goes to this combustion process goes.

In realistically every combustion goes through multiple reactions steps this reaction mechanism may involve few steps or even hundred steps or even thousand steps.

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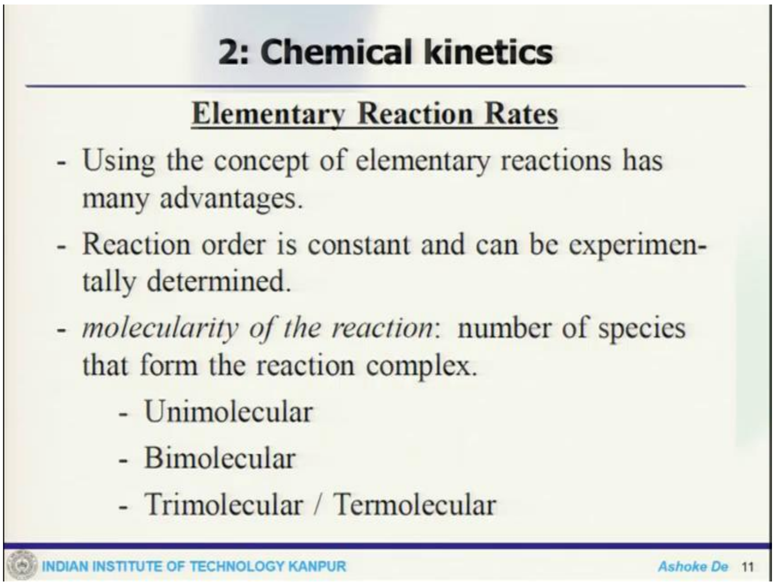

2: Chemical kinetics

Elementary Reaction Rates

- Using the concept of elementary reactions has many advantages.
- Reaction order is constant and can be experimentally determined.
- *molecularity of the reaction*: number of species that form the reaction complex.
  - Unimolecular
  - Bimolecular
  - Trimolecular / Termolecular

So, one has to look at the state of the art literature to see what are those things. Now our objectives to look at how we can find out the chemical timescale, so that is why this elementary reaction steps are very, very important and now using this concept all elementary reaction, you want to find out the chemical time scale. Reaction order is constant and can we determine another important thing is the molecularity of the reaction. So it could be Unimolar or it could be Bimolar or Trimolar.

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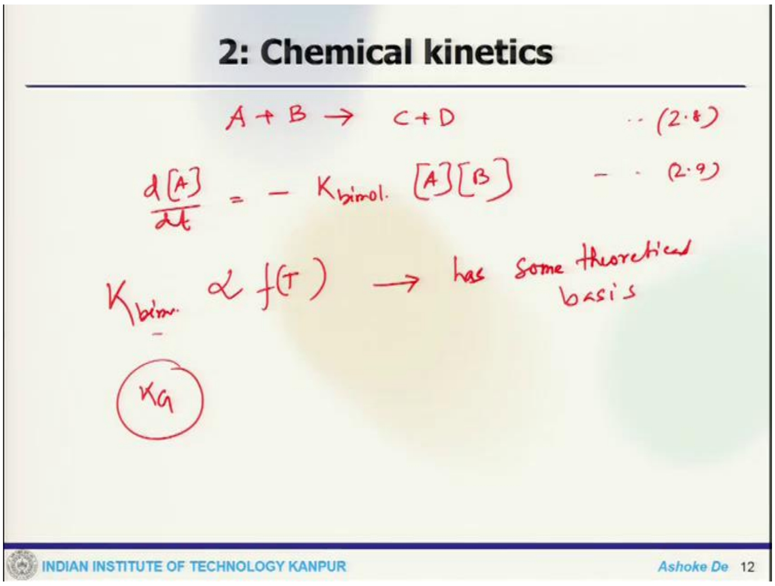

2: Chemical kinetics

$A + B \rightarrow C + D$ ·· (2.8)

$\frac{d[A]}{dt} = -K_{bimol.}[A][B]$ -- · (2.9)

$K_{bim.} \propto f(T) \rightarrow$ has some theoretical basis

K_G

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So, bimolar reaction for most of the combustion related to elementary reactions are bimolar that means there would be A + B which will form C + D so these are bimolar reaction and rate of reaction proceeds the reaction rate as:

$$\frac{d[A]}{dt} = -K_{bimol}[A][B]$$

This is the rate at which the bimolar reaction will proceed. So that means this $K_{bipolar}$ is proportional to function of some temperature and this has some theoretical basis.

Unlike K_G rate coefficient of global reaction. So this is the rate coefficient of global reaction which does not have that theoretical basis, but this bimolar reaction has not theoretical basis unlike K_G rate coefficient of global reaction and then this is the rate coefficient of global reaction which have that theoretical basis, but this bimolar reaction does not have theoretical basis of reaction and that comes from collision theory.

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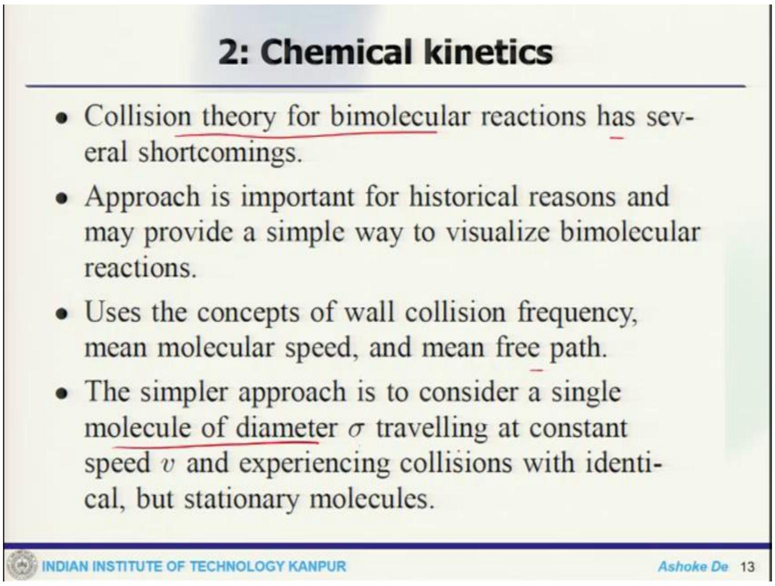

2: Chemical kinetics

- Collision theory for bimolecular reactions has several shortcomings.
- Approach is important for historical reasons and may provide a simple way to visualize bimolecular reactions.
- Uses the concepts of wall collision frequency, mean molecular speed, and mean free path.
- The simpler approach is to consider a single molecule of diameter σ travelling at constant speed v and experiencing collisions with identical, but stationary molecules.

But this collision theory of bimolar reaction that is another important thing one has to know that this has several shortcomings. So, the approach is quite important for historical reason and may provide a simple way to visualise the bimolar reaction, but uses the concept of wall collision frequency molecular speed mean free path. So, the simpler approaches to consider a single molecule of diameter Sigma travelling at constant speed v and experiencing the collision with inter identical but stationary molecules.

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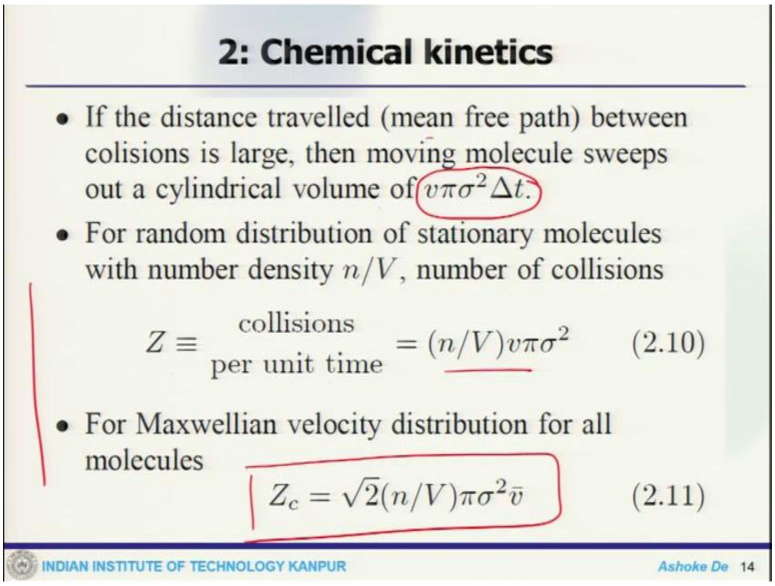

2: Chemical kinetics

- If the distance travelled (mean free path) between colisions is large, then moving molecule sweeps out a cylindrical volume of $v\pi\sigma^2\Delta t$.
- For random distribution of stationary molecules with number density n/V, number of collisions

$$Z \equiv \frac{\text{collisions}}{\text{per unit time}} = (n/V)v\pi\sigma^2 \qquad (2.10)$$

- For Maxwellian velocity distribution for all molecules

$$\boxed{Z_c = \sqrt{2}(n/V)\pi\sigma^2\bar{v}} \qquad (2.11)$$

The distance travelled that is the mean free path between collisions is large than the moving molecules without a cylindrical volume of this much. So, this is coming clearly from the collision theory and for the random distribution of the stationary molecules with number density (n/V) the number of collusion one can estimate at the collisions per unit time is $(n/V)\sigma^2$.

Now for Maxwell velocity distribution for all molecules this Z_c is coming from or statistical mechanics for where you get this.

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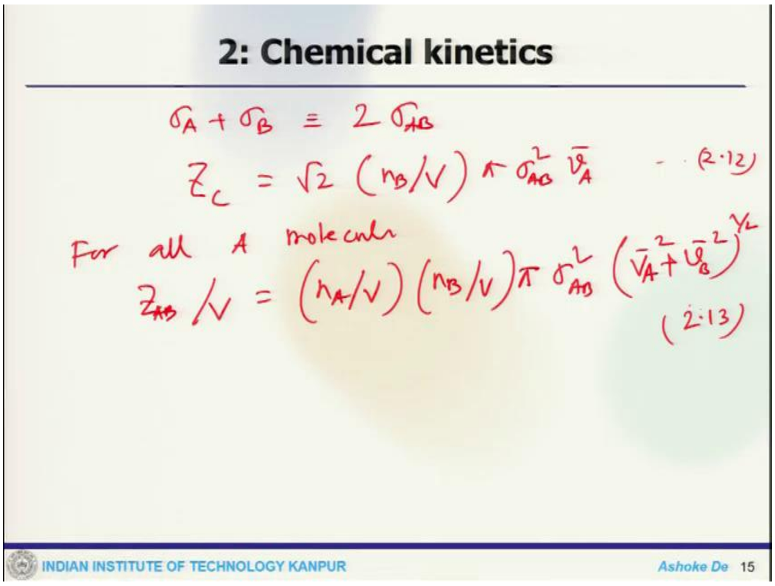

2: Chemical kinetics

$$\sigma_A + \sigma_B = 2\sigma_{AB}$$

$$Z_c = \sqrt{2}(n_B/V)\pi\sigma_{AB}^2\bar{\vartheta}_A \quad \text{-- (2.12)}$$

For all A molecule

$$Z_{AB}/V = (n_A/V)(n_B/V)\pi\sigma_{AB}^2(\bar{V}_A^2 + \bar{\vartheta}_B^2)^{1/2} \quad (2.13)$$

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Now when you go to that that 2.11 applies the identical molecules for different molecules, this should be:

$$\sigma_A + \sigma_B \equiv 2\sigma_{AB}$$

So my Z_c is going to be:

$$Z_c = \sqrt{2}\left({}^{n_B}/_{V}\right)\pi\sigma_{AB}^2\bar{\vartheta}_A$$

Which expresses the frequency of collision of a single A molecule with but now for all A molecules one can find out that:

$${}^{Z_{AB}}/_{V} = \left({}^{n_A}/_{V}\right)\left({}^{n_B}/_{V}\right)\pi\sigma_{AB}^2(\bar{\vartheta}_A + \bar{\vartheta}_B)^{1/2}$$

So, that is what you get, so I will stop here today and continue the discussion in the next lecture.