Turbulent Combustion: Theory and Modelling
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Lecture – 8
Chemical Kinetics (Contd.,)

Welcome back. So let us continue the discussion on chemical kinetics and this is where exactly stopped.

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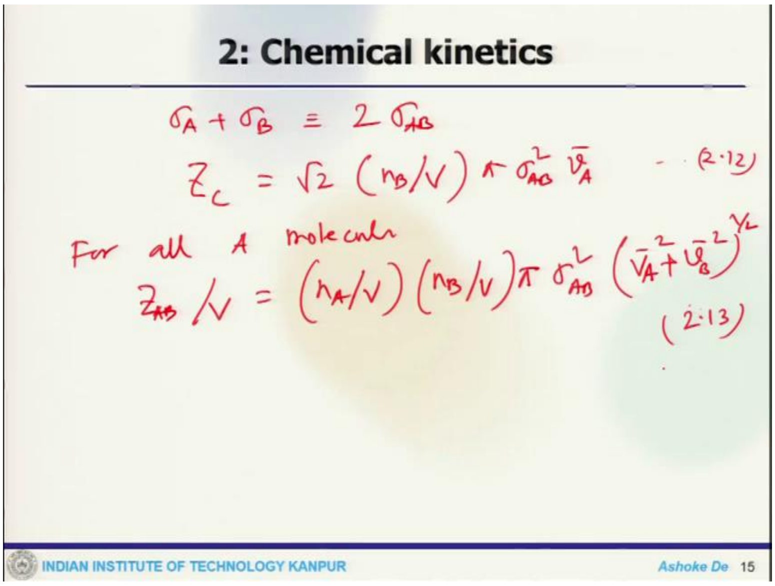

2: Chemical kinetics

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

$$Z_c = \sqrt{2}\,(n_B/V)\,\pi\,\sigma_{AB}^2\,\bar{v}_A \quad \cdots (2.12)$$

For all A molecule

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

When talking the collision frequency from the molecular level. This is exactly the expression where we stop for these things.

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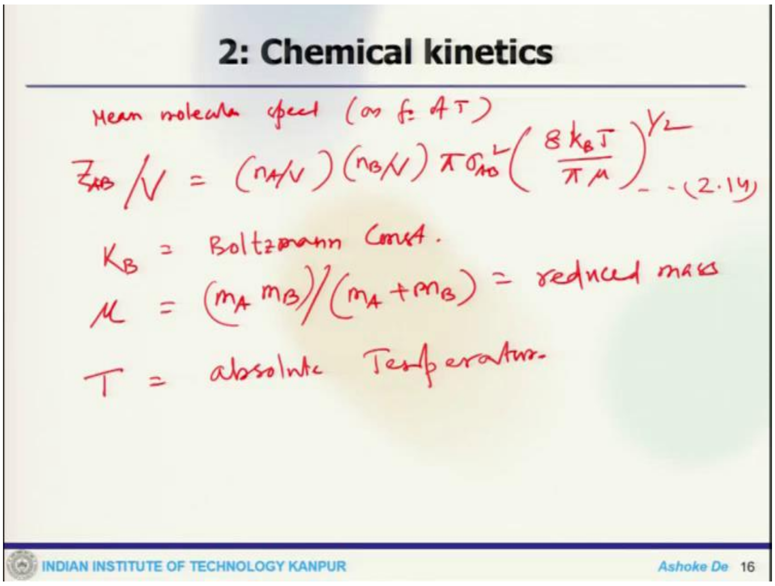

2: Chemical kinetics

Mean molecula speed (as f: of T)

$$Z_{AB}/V = (n_A/V)(n_B/V)\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \quad --(2.14)$$

K_B = Boltzmann Const.

$\mu = (m_A m_B)/(m_A + m_B)$ = reduced mass

T = absolute Temperature

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Now, one can estimate the expression for mean molecular speeds so the mean in terms of temperature as a function of temperature. So, we can write:

$$Z_{AB}/_V = (n_A/_V)(n_B/_V)\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

That is our 2.14. Now this is where your kinetic theory comes into the picture. So, this k_B is Boltzmann constant, this is Boltzmann constant and μ is:

$$\mu = (m_A m_B)/(m_A + m_B)$$

which is the reduced mass. So, one can think about that way and T is absolute temperature.

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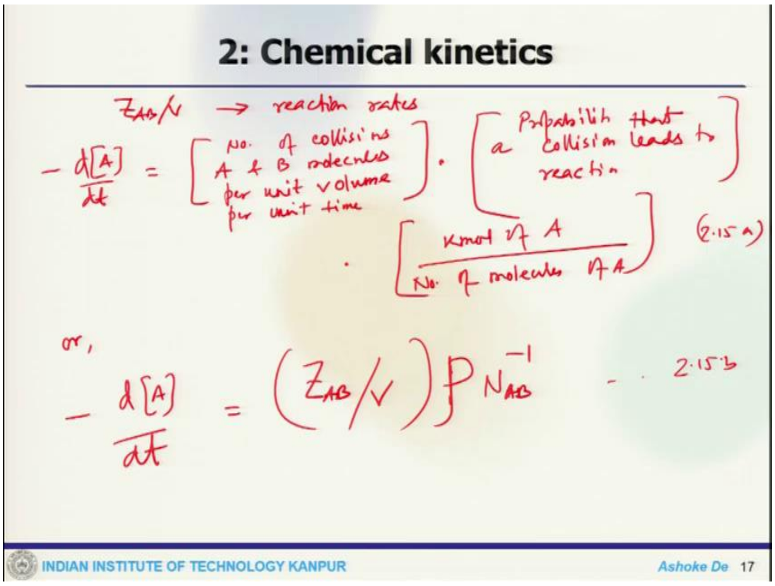

2: Chemical kinetics

Z_{AB}/V → reaction rates

$$-\frac{d[A]}{dt} = \left[\begin{array}{c}\text{No. of collisions}\\ \text{A \& B molecules}\\ \text{per unit volume}\\ \text{per unit time}\end{array}\right] \cdot \left[\begin{array}{c}\text{a Probability that}\\ \text{collision leads to}\\ \text{reaction}\end{array}\right] \cdot \left[\frac{\text{kmol of A}}{\text{No. of molecules of A}}\right] \quad (2.15a)$$

or,

$$-\frac{d[A]}{dt} = (Z_{AB}/V)\,\rho\, N_{AB}^{-1} \quad --\ 2.15b$$

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Now also you can relate this $\left(Z_{AB}/_{V}\right)$ to the reaction rate and that should $\left(d[A]/_{dT}\right)$ equals to number of collision A and B molecules per unit volume per unit time multiply by the probability that a collision leads to reaction multiply by kilo mole of A to the number of molecules of A which is this. So, one can simplify this like:

$$-\frac{d[A]}{dt} = \left(Z_{AB}/_{V}\right) P_{N_{AB}}^{-1}$$

So that is the probability you can get.

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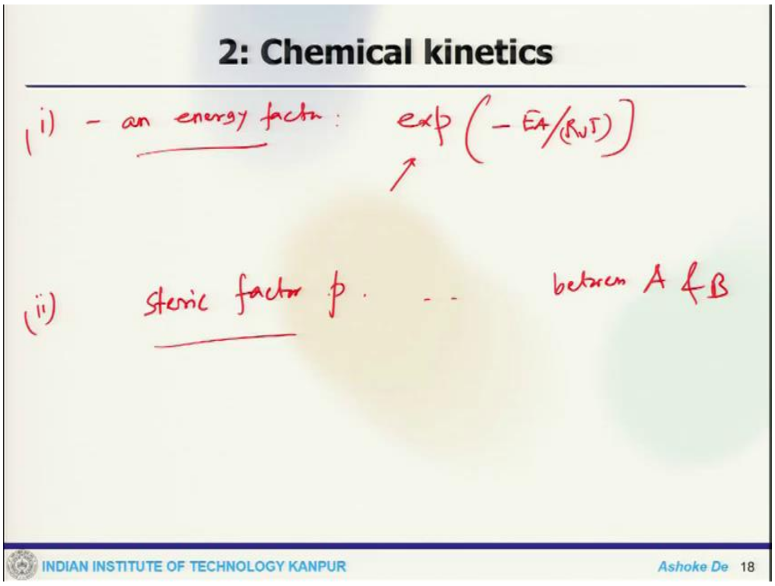

2: Chemical kinetics

i) - an energy factor : $\exp\left(-E_A/(R_U T)\right)$

(ii) steric factor p . . . between A & B

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Now the probability that collusion will lead to a reaction can also be expressed as a product of two factors. One is an energy factor, so which is kind of:

$$\exp({}^{-E_A}/_{R_U T})$$

which actually this guy expresses the fraction of collision that occur within energy above the activation energy. This is the factor number 1 and factor number 2, its geometrical or one someone call it is a steric factor p.

So, that takes into account the geometry of collision between A and B. So, this is a geometric factor. When is the energy factor which actually takes into account the function of collision that occur with the energy of the activation energy or second geometry factor that is taking it considered.

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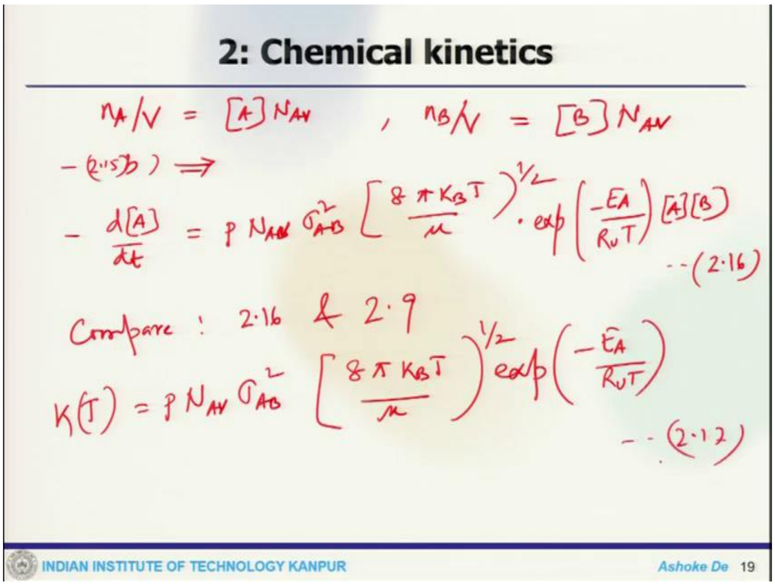

2: Chemical kinetics

$n_A/V = [A]N_{AV}$, $n_B/V = [B]N_{AV}$

– (2.15b) ⇒

$$-\frac{d[A]}{dt} = p N_{AB} \sigma_{AB}^2 \left[\frac{8\pi K_B T}{\mu}\right)^{1/2} \cdot exp\left(\frac{-E_A}{R_u T}\right)[A][B] \quad --(2.16)$$

Compare : 2.16 & 2.9

$$K(T) = p N_{AV} \sigma_{AB}^2 \left[\frac{8\pi K_B T}{\mu}\right)^{1/2} exp\left(-\frac{E_A}{R_u T}\right) \quad --(2.12)$$

Now substitution of $\left({}^{n_A}/_{V}\right)$ with $[A]N_{AV}$ and $\left({}^{n_B}/_{V}\right)$ as $[B]N_{AV}$ into the equation 2.15 b becomes:

$$-\frac{d[A]}{dt} = PN_{AB}\sigma_{AB}^2\left[\frac{8\pi K_B T}{\mu}\right]^{1/2} exp\left(\frac{-E_A}{R_U T}\right)[A][B]$$

So this is your 2.16. So, if you compare 2.16 and 2.9 what you get this:

$$k(T) = PN_{AB}\sigma_{AB}^2\left[\frac{8\pi K_B T}{\mu}\right]^{1/2} exp\left(\frac{-E_A}{R_U T}\right)$$

So by comparing you can find out that reaction coefficient to these things.

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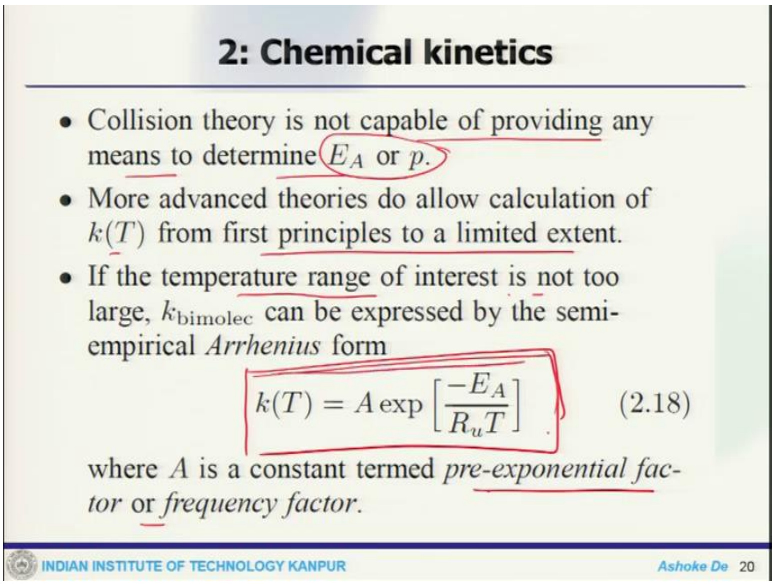

2: Chemical kinetics

- Collision theory is not capable of providing any means to determine E_A or p.
- More advanced theories do allow calculation of $k(T)$ from first principles to a limited extent.
- If the temperature range of interest is not too large, k_{bimolec} can be expressed by the semi-empirical *Arrhenius* form

$$\boxed{k(T) = A\exp\left[\frac{-E_A}{R_u T}\right]} \qquad (2.18)$$

where A is a constant termed *pre-exponential factor* or *frequency factor*.

Now one may look at this collision theory that it is not capable of providing any means to determine A and B. So, collision theory that so that means one need some more advanced theories to allow calculation of k(T) from first principle to a limited extend. Now if the temperature is not that large are the temperature range that is considered or of interest is not too large then this bimolar constant can be expressed by the semi empirical Arrhenius form. That means this k(T) can be expressed as:

$$k(T) = Aexp\left[\frac{-E_A}{R_uT}\right]$$

Where A is the pre-exponential factor or frequency factor for different book actually uses different terminology. So, what essentially you get to see the big expression of 2.17 for a particular range of interest you get when Arrhenius expression which looks much more simplified in that sense. And this is what pretty much if you have an idea about combustion of basics of combustion in a reaction kinetics talk about Arrhenius expression that comes for this basis.

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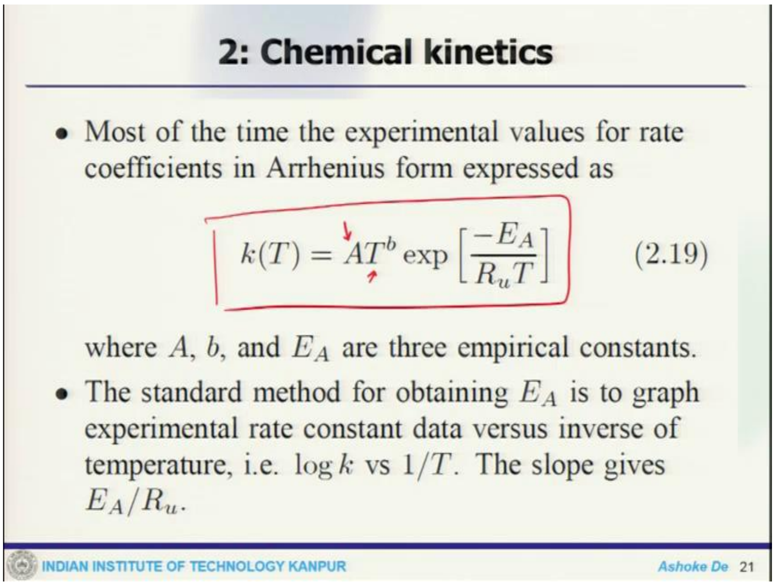

2: Chemical kinetics

- Most of the time the experimental values for rate coefficients in Arrhenius form expressed as

$$\boxed{k(T) = AT^b \exp\left[\frac{-E_A}{R_uT}\right]} \qquad (2.19)$$

where A, b, and E_A are three empirical constants.

- The standard method for obtaining E_A is to graph experimental rate constant data versus inverse of temperature, i.e. $\log k$ vs $1/T$. The slope gives E_A/R_u.

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What happened most of the time this experimental values of the rate coefficients in expressed within another factor taking into consideration the temperature exponent. So, that K is represented completely within P exponential factor in the temperature exponent and activation energy component. So, these are the particular reactions so the standard method for finding this is EA is the exponential rate constant data when you plot it so that the slope which will give you this.

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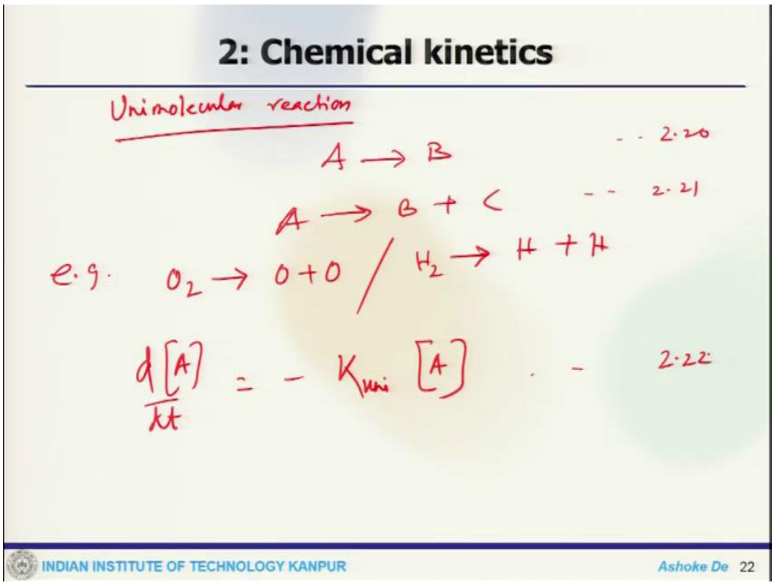

2: Chemical kinetics

Unimolecular reaction

$$A \rightarrow B \quad \text{-- } 2.20$$

$$A \rightarrow B + C \quad \text{-- } 2.21$$

e.g. $O_2 \rightarrow O + O$ / $H_2 \rightarrow H + H$

$$\frac{d[A]}{dt} = -K_{uni}[A] \quad \text{-- } 2.22$$

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Now from the bimolar reaction you come to the Uni molecular reaction. So, Uni molecular reaction that means A goes to B or A goes to B + C for example one can think about O_2 goes to O + O or H_2 goes to H + H, so these are your equation number. First order at high pressure one can find out the reaction rate:

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

Ao that is how you estimate the reaction rate. Now that is at high pressure.

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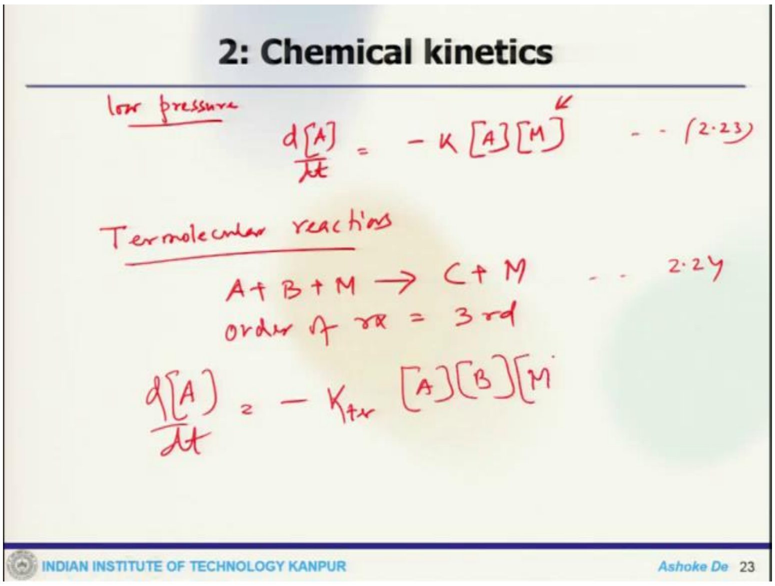

2: Chemical kinetics

low pressure

$$\frac{d[A]}{dt} = -K[A][M] \quad \text{-- } (2.23)$$

Termolecular reactions

$$A + B + M \rightarrow C + M \quad \text{-- } 2.24$$

order of rx = 3rd

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

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Now that means now that when you commit that something happening at the high pressure then there must be something which happens at low pressure also. Now when you go to low pressure so the reaction that also depend on third molecule that may exit from reaction volume in that case this would be:

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

So, this the third molecule I am talking about and that is how is you get uni molecular reaction step. Now other one is that one is the tri molecular or termolecular reactions. Here A + B + M goes to C + M the order of reaction here is 3rd order. So, one can find out the reaction rate, so that is how whether it is a Uni molecular bimolecular or tri molecular. Most of the reactions are usually limited reactions are bimolecular.

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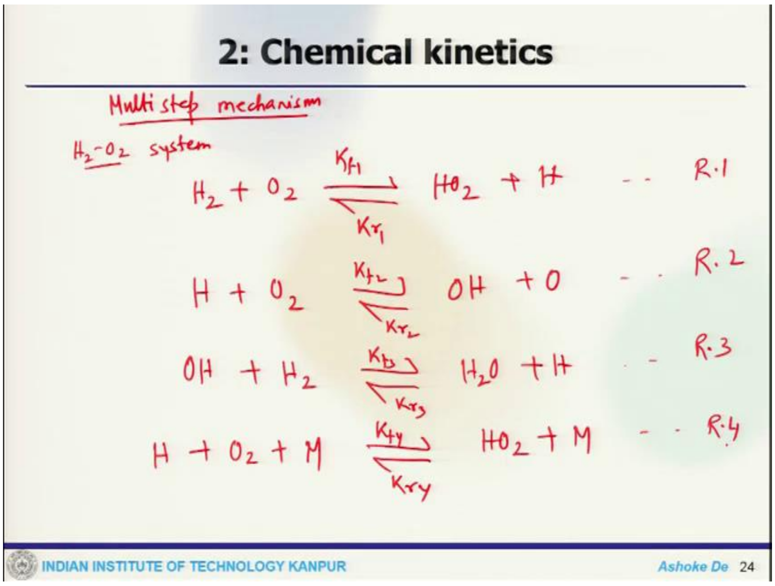

2: Chemical kinetics

Multi step mechanism

H_2-O_2 system

$H_2 + O_2 \underset{K_{r_1}}{\overset{K_{f_1}}{\rightleftharpoons}} HO_2 + H$ -- R.1

$H + O_2 \underset{K_{r_2}}{\overset{K_{f_2}}{\rightleftharpoons}} OH + O$ -- R.2

$OH + H_2 \underset{K_{r_3}}{\overset{K_{f_3}}{\rightleftharpoons}} H_2O + H$ -- R.3

$H + O_2 + M \underset{K_{r_4}}{\overset{K_{f_4}}{\rightleftharpoons}} HO_2 + M$ -- R.4

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Now you can look at the multi step mechanism. So, in the multistep mechanism used to find out the net production rate. So let us consider this example of H_2-O_2 system if you considered this is H_2-O_2 system. So, you can write in H2 + O2 so this is K_{f1} goes to HO_2 + H, K_{r1} so that means this is R1 reaction one. So, reaction 1: H_2, O_2 goes to HO_2, this is forward coefficient is forward collision. K_{r1} is the reverse coefficient similarly H + O_2 K_{f2} to OH + O K_{r2} this is your reaction 2 and the third one will be OH + H_2 to H_2O goes to K_{f3} and reverse form would be H_2O and H that is K_{r3}. So this is R3.

And the last one is H + O_2 + M which goes to K_{f4} which is K_{r4}, so HO_2 + M goes to R4. So, these are the different multiple step or elementary step that you have and you get those forward and every action state has forward direction and reverse direction. So, we can find out the forward and reverse these things.

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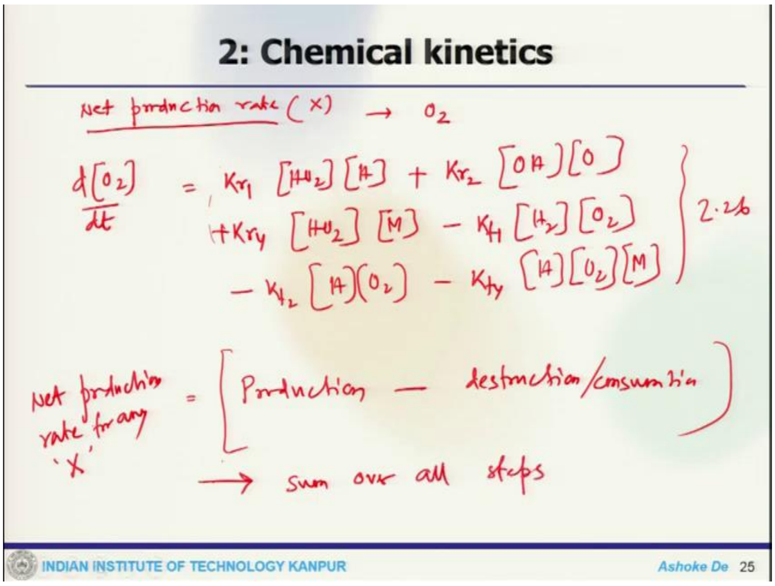

2: Chemical kinetics

Net production rate (X) → O_2

$$\frac{d[O_2]}{dt} = K_{r_1}[HO_2][H] + K_{r_2}[OH][O] + K_{r_4}[HO_2][M] - K_{f_1}[H_2][O_2] - K_{f_2}[H](O_2) - K_{f_4}[H][O_2][M] \quad 2.26$$

Net production rate for any 'X' = [Production − destruction/consumption]

→ sum over all steps

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Now, the net production rate of any species let us say X involving the sum of all the individual. Now, we are trying to find out the net production rate. So, you try to find out it is an x inverse is sum of the all individual elementary reaction producing and x minus all the distance. Essentially when you try to find out the net production rate for x, for example, if you want to find out the net production rate of O, then we have to consider those particular reactions.

For example reaction 2, it is involved let say instead of taking that we take OH. So, OH is involved in reaction 2, OH is involved here. So these two reactions should be considered. And if you look at reaction 2, OH is produced here, other case OH is getting destroyed here. So the combination of that would give you the net production rate for a particular species or element x.

So, for example, let us say we want to find out net production rate for O_2 then this could be $\frac{d[O_2]}{dt}$. So O_2 is involved fast reaction second reaction and last reaction. First reaction it is K_{r1} $[HO_2]$ [H]+ K_{r2} [OH] [O], so that is where this is forming then K_{r4} [H] $[O_2]$ [M]. Fourth reaction it is forming minus K_{f1} $[H_2]$ $[O_2]$ – K_{f2} $[HO_2]$ – K_{f4} $[HO_2]$ [M], so as I said the net production rates, these are the reactions step here and here these are produced and then these reactions in the forward direction oxygen is also consumed.

So, to find out the net production rate first we considered the producing part then subtracting from the reverse part. So, the total production minus destruction or conjunction this is your net production rate for any x this should go and it is some over all states like for example oxygen that is what we get.

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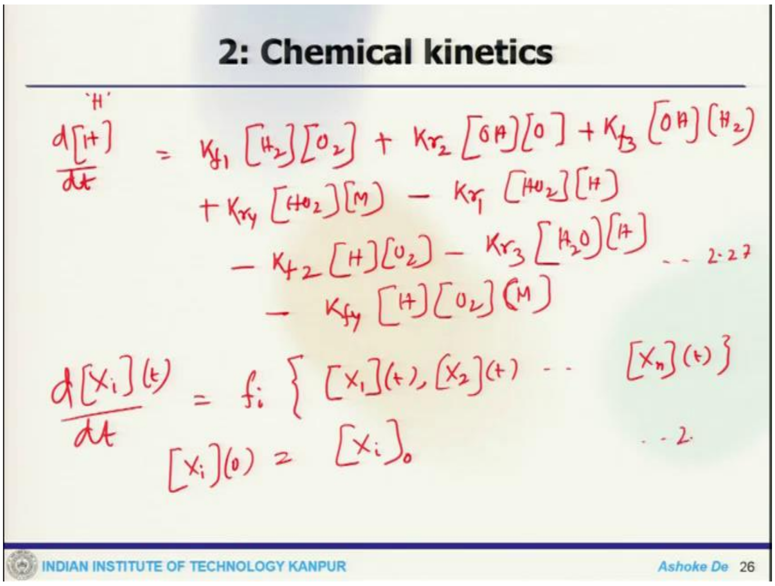

2: Chemical kinetics

'H'

$$\frac{d[H]}{dt} = K_{f1}[H_2][O_2] + K_{r2}[OH][O] + K_{f3}[OH][H_2] + K_{r4}[HO_2][M] - K_{r1}[HO_2][H] - K_{f2}[H][O_2] - K_{r3}[H_2O][H] - K_{f4}[H][O_2][M] \quad \ldots 2.27$$

$$\frac{d[X_i](t)}{dt} = f_i\{[X_1](t), [X_2](t) \ldots [X_n](t)\}$$

$$[X_i](0) = [X_i]_0 \quad \ldots 2.$$

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Similarly we can write for H it is:

$$\frac{d[H]}{dt} = K_{f1}[H_2][O_2] + K_{r2}[OH][O] + K_{f3}[OH][H_2]+K_{r4}[HO_2][M] - K_{r1}[HO_2][H] - K_{f2}[H][O_2] - K_{r3}[H_2O][H] - K_{f4}[H][O_2][M]$$

So this is how you get it. So, for any particular species one can write that:

$$\frac{d[X_i](t)}{dt} = f_i\{[X_1](t), [X_2](t) \ldots [X_n](t)\}$$

So that is how you can generalise for a particular species with.

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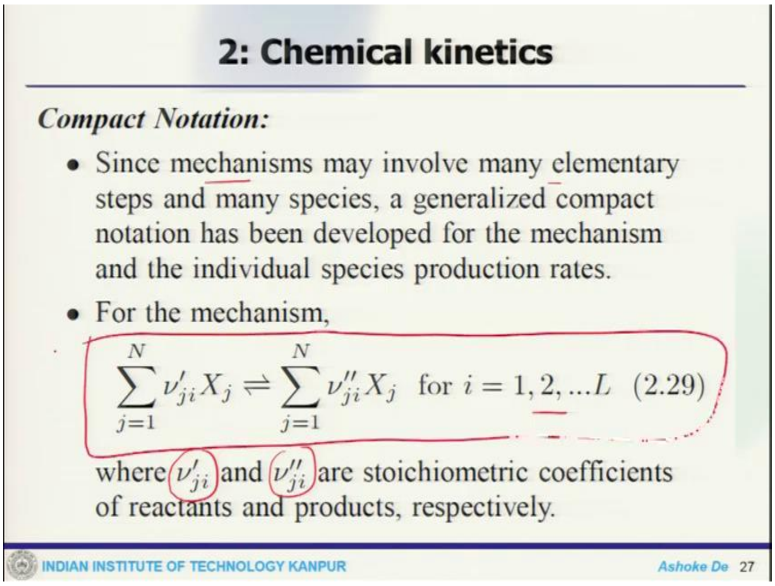

2: Chemical kinetics

Compact Notation:

- Since mechanisms may involve many elementary steps and many species, a generalized compact notation has been developed for the mechanism and the individual species production rates.
- For the mechanism,

$$\sum_{j=1}^{N} \nu'_{ji} X_j \rightleftharpoons \sum_{j=1}^{N} \nu''_{ji} X_j \quad \text{for } i = 1, 2, \ldots L \quad (2.29)$$

where ν'_{ji} and ν''_{ji} are stoichiometric coefficients of reactants and products, respectively.

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So, one can sum up of those things and put it in a compact notation. So if your reaction steps are the chemical mechanism involve elementary steps and many species is generally light compact notation can be developed for the mechanism. So, the mechanism let us say there are n steps and n number of species which are involved so that goes from this is the forward direction.

And this is the reverse direction and this is the stoichiometric coefficient is reversed stoichiometric coefficient and it is generic form one can write these many of moles.

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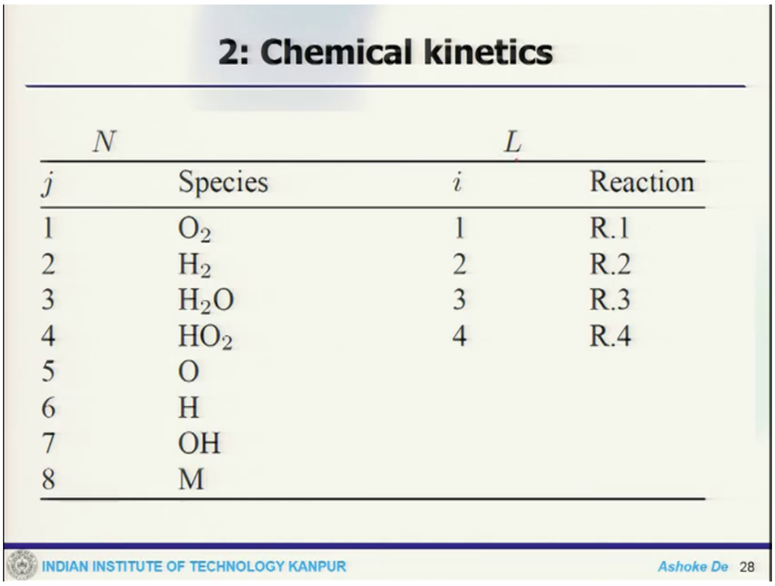

2: Chemical kinetics

N		L	
j	Species	i	Reaction
1	O_2	1	R.1
2	H_2	2	R.2
3	H_2O	3	R.3
4	HO_2	4	R.4
5	O		
6	H		
7	OH		
8	M		

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For example that we have taken there are number of species are O_2, H_2, H_2O, HO_2, OH and this and number of reaction steps are 4 this is how this is here. So, that the loop it goes over.

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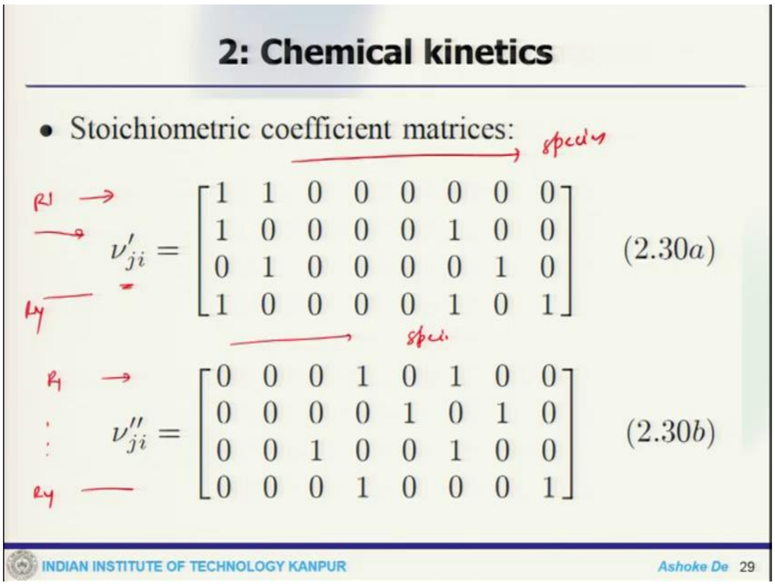

2: Chemical kinetics

- Stoichiometric coefficient matrices:

species

$$\begin{array}{cc} R1 & \\ & \\ & \nu'_{ji} = \\ R4 & \end{array} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \quad (2.30a)$$

spec.

$$\begin{array}{cc} R1 & \\ & \nu''_{ji} = \\ & \\ R4 & \end{array} \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (2.30b)$$

And if you look at the Stoichiometric coefficient matrix, this is how it looks like this is the forward Stoichiometric coefficient. So those who are sitting in the every row is your reaction step and 1 to 8 so 0, 1, 2, 3, 4, 5, 6, 7, 8 so this are going for species, so every step which are the species they are sitting there in the forward direction will be here R1 raised to 0. It is similar in the reverse direction this is corresponding reaction 1 to reaction 4 and this is species in this direction. So that is the way the matrix is formed.

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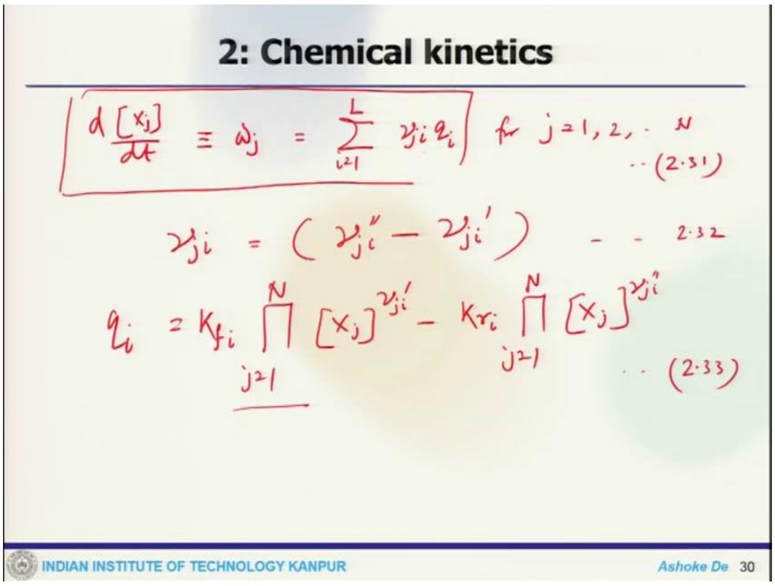

2: Chemical kinetics

$$\boxed{\frac{d[X_j]}{dt} \equiv \dot{\omega}_j = \sum_{i=1}^{L} \nu_{ji} q_i} \quad \text{for } j = 1, 2, \ldots N \quad \cdots (2.31)$$

$$\nu_{ji} = (\nu''_{ji} - \nu'_{ji}) \quad - - \ 2.32$$

$$q_i = k_{fi} \prod_{j=1}^{N} [X_j]^{\nu'_{ji}} - k_{ri} \prod_{j=1}^{N} [X_j]^{\nu''_{ji}} \quad \cdots (2.33)$$

Now once that is formed so for a multistage mechanism the net production rate let us say this species is $\dot{\omega}_j$ which is going over all the reactions step ϑ_{ji} and q_i for j goes from 1 to n, so this is your equation where ϑ_{ji} is the difference between your reverse stoichiometric coefficients to the forward stoichiometric coefficient. So, that is how you put them together and q_i is your forward reaction rate minus reverse rate. So, essentially what we are showing a different example like production ratio.

Now this is more in the compact form and in the compact form. you have; so that is for individual species in j and any individual species at j you get the reaction rate and the reaction rate summation over all the reactions state with ϑ_{ji} and q_i. And q_i contains the; this is your forward direction and the reverse directions that will essentially take care of your production and the destruction of that particular individual species. This is how in a general form you can write it.

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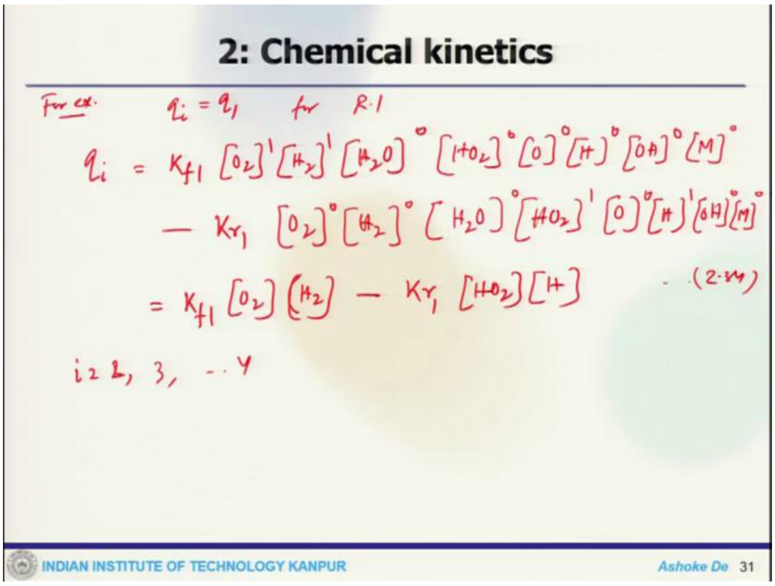

2: Chemical kinetics

For ex. $q_i = q_1$ for R.1

$$q_i = K_{f1}[O_2]^1[H_2]^1[H_2O]^0[HO_2]^0[O]^0[H]^0[OH]^0[M]^0$$
$$- K_{r1}[O_2]^0[H_2]^0[H_2O]^0[HO_2]^1[O]^0[H]^1[OH]^0[M]^0$$
$$= K_{f1}[O_2][H_2] - K_{r1}[HO_2][H] \quad \ldots (2.34)$$

$i = 2, 3, \ldots 4$

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Now you see how this generic things actually work for example you take q_i equals to q_1 for R1 then q_i is:

$$q_i = K_{f1}[O_2]'[H_2]'[H_2O]^0[HO_2]^0[O]^0[H]^0[OH]^0[M]^0$$
$$- K_{r1}[O_2]^0[H_2]^0[H_2O]^0[HO_2]'[O]^0[H]'[OH]^0[M]^0$$

So, which is:

$$= K_{f1}[O_2][H_2] - K_{r1}[HO_2][H]$$

So Sigma expression one can write for i equals to 2, 3 and 4 since it is simple H_2-O_2 mechanism and you have limited number of species you can actually write all the individual expression and see how they are correlated compact notation.

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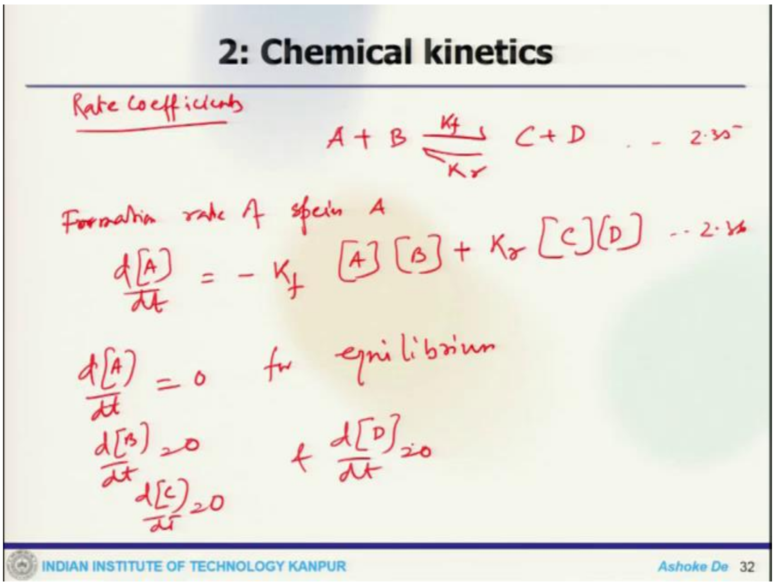

2: Chemical kinetics

Rate Coefficients

$$A + B \underset{K_r}{\overset{K_f}{\rightleftharpoons}} C + D \quad \ldots \; 2.35$$

Formation rate of species A

$$\frac{d[A]}{dt} = -K_f [A][B] + K_r [C][D] \quad \ldots \; 2.36$$

$$\frac{d[A]}{dt} = 0 \quad \text{for equilibrium}$$

$$\frac{d[B]}{dt} = 0 \quad \& \quad \frac{d[D]}{dt} = 0$$

$$\frac{d[C]}{dt} = 0$$

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Now the other thing is the finding the rate coefficients and equilibrium constants. So, equilibrium forward and reverse reaction rates must be equal. So for example A + B which is the forward reaction? This should be same so the formation rate of species for example formation rate of species A is:

$$\frac{d[A]}{dt} = -K_f[A][B] + K_r[C][D]$$

So, for equilibrium time rate of change of a must be zero. Same is true for essentially $\frac{d[A]}{dt}$ is 0 for equilibrium and that is true for other also $\frac{d[A]}{dt}$ 0, $\frac{d[A]}{dt}$ 0 and $\frac{d[A]}{dt}$ 0, so maintain the equilibrium this thing needs to go to 0.

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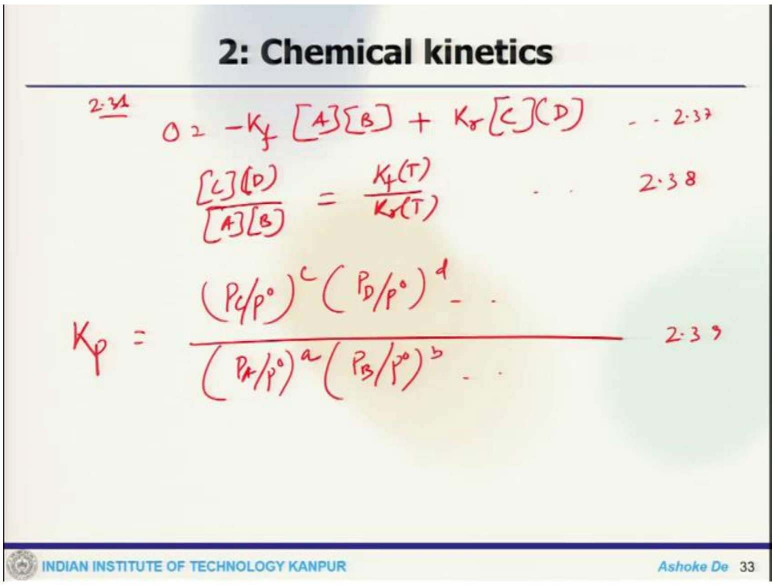

2: Chemical kinetics

2.36

$$0 = -K_f [A][B] + K_r [C][D] \quad \ldots 2.37$$

$$\frac{[C][D]}{[A][B]} = \frac{K_f(T)}{K_r(T)} \quad \ldots 2.38$$

$$K_p = \frac{(P_C/P^\circ)^c (P_D/P^\circ)^d \ldots}{(P_A/P^\circ)^a (P_B/P^\circ)^b \ldots} \quad 2.39$$

So, now equation 2.36 one can get:

$$0 = -K_f [A][B] + K_r [C][D]$$

So which is if you rearrange this it should be:

$$\frac{[C][D]}{[A][B]} = \frac{K_f}{K_r}$$

So we have already define the equilibrium constant as:

$$K_p = \frac{\left({P_C}/{P^0}\right)^c \left({P_D}/{P^0}\right)^d}{\left({P_A}/{P^0}\right)^a \left({P_B}/{P^0}\right)^b}$$

So, this is how you are defined it now molar concentration can be related to the mole fraction and that will actually look at it in the next lecture, we will stop here.