Lecture – 9
Chemical Kinetics (Contd.,)

Welcome back. Let us continue the discussion on the kinetics. So we are looking at a global reaction and the multistep mechanism like the reaction which course to multiple elementary reaction. And then from there, once you look at the elementary reaction. There are multiple species are the radicals which are formed during this elementary process and using those and the concept of equilibrium when trying to find out the rate constant.

(Refer Slide Time: 00:51)

So, where we actually stopped in our discussion is that finding this using the concept of equilibrium and you correlate the equilibrium constant from the partial pressure.

(Refer Slide Time: 01:12)

We can find out the molar concentration which can be related to mole fraction and partial pressure. So, this is my molar concentration which can be related to that which is nothing but $\left(P_i/R_uT\right)$, so here the molar concentration is actually connected with the partial pressure and mole fraction. Now, we can define the equilibrium constant based on the molar concentration like K_c related to K_p.

So, we can find out:

$$K_p = K_c \left(R_uT/P^0\right)^{c+d-a-b}$$

which is 2.41a or one can find out:

$$K_p = K_c \left(R_uT/P^0\right)^{\sum v''-v'}$$

So, you can actually correlate the rate constant.

(Refer Slide Time: 02:39)

And now we can find out of the K_c. So, the K_c is:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Which is a product of X_i divided by product of reactant and this is equation 2.42. So, that you get:

$$\frac{K_f(T)}{K_r(T)} = K_c(T)$$

So that will get you equation 2.43. For bimolecular reaction K_c is nothing but K_p so this is what you get.

**(Refer Slide Time: 04:00)**

Now there are some approximations which are very common in this equilibrium analysis is the steady state approximation. So, for the steady state approximation talks about or this is the analysis of any reactive system which can be simplified by applying the steady state approximation to the reactive species of the radicals because as we have seen the intermediate reactants. And we get all these radicals and using the steady state approximation we can find out these details.

Steady State also justified when the reaction forming the intermediate species is slow while the reaction destroying the intermediate species very fast. That means whatever is formed it is getting consumed at a faster rate. So this is quite a good for approximation. So, the result of that is the concentration of the radical is small in comparison with those of the reactants and products.

(Refer Slide Time: 05:10)
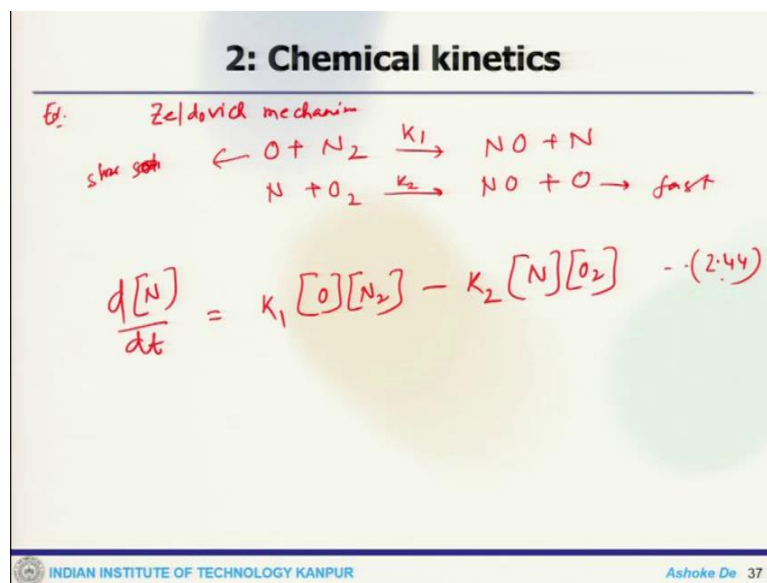
So, what we can take and again and example, for example, NO formation mechanism is very well known is the Zeldovich mechanism. So, we take that for NO formation, you have $O + N_2$ the faster with forms $NO + N$, $N + O_2$ to form $NO + O$. So, here this fast reaction is slow and rate limiting. But the second one is quite fast now if one has to look at the net production rate of atoms so this will be:

$$\frac{d[N]}{dt} = K_1[O][N_2] - K_2[N][O_2]$$

So this is what you get so that means in particular step.

(Refer Slide Time: 06:23)

Now if you allow the rapid transient to build up the N, so your $\left(d[N]/dt\right)$ will approach to zero, which means this if I correlate this should be:

$$0 = K_1[O][N_2] - K_2[N][O_2]$$

So my [N] at steady state is:

$$[N]_{SS} = \frac{K_1[O][N_2]}{K_2[O_2]}$$

So this you can mark as 2.45 and this is 2.46. Now the time rate of change of $[N]_{SS}$ is:

$$\frac{d[N]_{SS}}{dt} = \frac{d}{dt}\left[\frac{K_1[O][N_2]}{K_2[O_2]}\right]$$

So that one can find out by taking the derivative of that thing. So, this is how one can using the steady state approximation and find out all these details.

Now we can move to the; what happens when you have a uni-molecular reaction so, we will look for uni-molecular reaction. So fast consider or let us consider three step mechanism, for example A + M which goes to A* + M then use take A* + M which goes A + M then finally K Uni molecular to products. So, essentially these are your 2.48 (a to c). So, first step of step 1 what you do? So the kinetic energy which is transferred to A from M, A has increased internal vibrational and rotational energy and becomes energies a molecule to A*.

Because of this, you get to possible scenarios for A*. So there are 2 possible scenarios for A*, so number one A star may collide with another molecule and goes back to A which is actually happening at this step. Here where A* is colliding with another molecule and goes back to A,

or what may possibly happen if A* may decompose into products which is essentially this step. Whereas A* is actually decomposed to a product. Now one can find out the rate at which the products are formed.

So this should be products equals to K_{uni} molecular reaction to A*. Now the net production of A* is:

$$\frac{d[A^*]}{dt} = K_e[A][M] - K_{dt}[A^*][M] - K_{uni}[A^*]$$

So this is where you get your Net production rate for A*.

(Refer Slide Time: 11:15)

Now we apply the steady state approximation for A* which will be:

$$\frac{d[A^*]}{dt} = 0$$

Fom there, we get the concentration for A* is:

$$[A^*] = \frac{K_e[A][M]}{K_{dt}[M] - K_{uni}}$$

So this is what you get, now, we substitute equation 2.51 into 2.49 what we get:

$$\frac{d(Products)}{dt} = \frac{K_e[A][M]}{\left(\frac{K_{dt}}{K_{uni}}\right)[M] + 1}$$

So, that is what you get for the products rate.

Now, one can write in a different form for the overall rate of production of the product where your A is going to products that is through this reaction. So, one may write like:

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

This is alternative way of writing the production of product. So, K$_{app}$ is nothing but the apparent unimolecular rate now we equate two equation 2.52 and 2.54 which will yield that:

$$K_{app} = \frac{K_e[M]}{\left(K_{dt}/K_{uni}\right)[M] + 1}$$

Which is equation 2.55.

Now 2.5, let us explain this previous equation 2.55 explain pressure dependence of unimolecular reaction. Now your pressure is high enough. So, that means:

$$\left(K_{de}[M] / K_{uni} \right) \gg 1$$

Because [M] increases as the pressure is increased. So, what will happen when:

$$K_{app}(p \to \infty) = K_{uni} {}^{K_e} / K_{de}$$

Which is your equation 2.56. Now, this is your situation where you have high enough pressure. Now if your pressure is low. So, for low enough pressure there are two different condition.

So, what again we can say that this term is very much less than 1 so that means:

$$K_{app}(p \to 0) = K_e[M]$$

So for two different condition or the two different pressure dependency that thing you can find out what would be the thing.

(Refer Slide Time: 16:03)
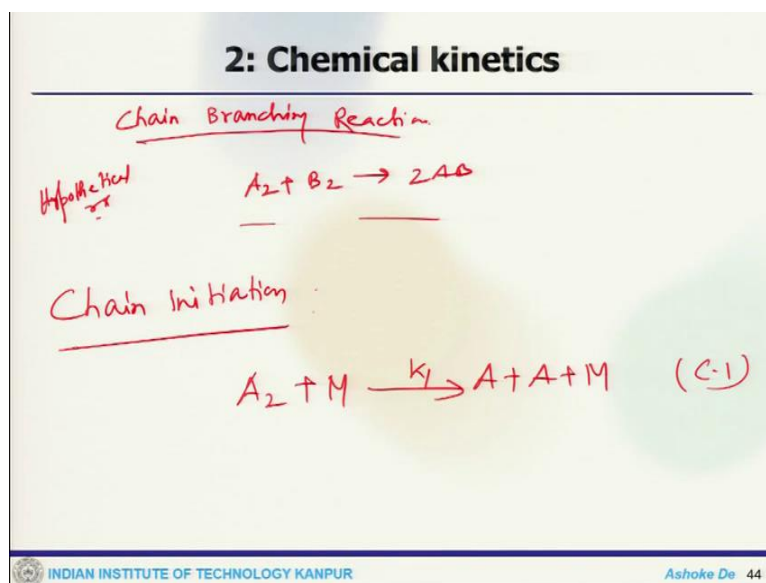
Now, I have another important thing when you look at the element reactions are the chain branching reaction. So, chain branching reaction, chain reaction actually one or more radical or the species that subsequent react to the React to produce any other radical. So that means in the reaction so some more feature of chain reaction we consider a hypothetical let say chain reaction. Let say $A_2 + B_2$ which becomes 2AB.

Now this is a hypothetical global reaction. Now the chain reaction of this that will be multiple steps of the chain reaction there will be fast step which is call chain initiation that means A_2 + M which will give A+ A+ M so that is your first step.

(Refer Slide Time: 17:17)
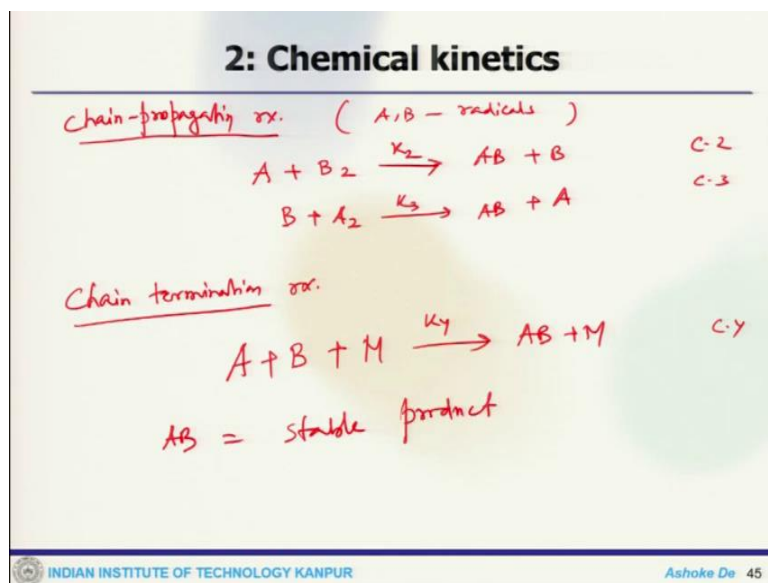
Now we will get what is the initiation takes place there would be chain propagating reaction. So, chain propagating reaction will involve, so free radicals like A and B so that means it will go A + B_2 to AB + B with K_2 so that is C2, B + A_2 which will go to AB + A which is C3, so one you first get the chain initiation. After initiation, there is a propagating reaction which will actually form the radical essentially A, B this radicals are formed. So, now you go to chain termination reaction.

So, chain termination reaction means the whole chain with got initiated that will be now terminated for this particular reaction now, you got M which will K4 + AB + M so, where AB is more like stable product. Now in the termination state you get in stable product like that.

So, the concentration of A and B are quite small throughout the course of reaction. So, AB at initial stages that one can ignore the reverse reactions and we can find out the reaction rate for this stable species like A_2 and B_2 which are:

$$\frac{d[A_2]}{dt} = -K_1[A_2][M] - K_3[A_2][B] \text{ and } \frac{d[B_2]}{dt} = -K_2[B_2][A]$$

And then finally you get the product species:

$$\frac{d[AB]}{dt} = K_2[A][B_2] + K_3[A_2][B] + K_4[A][B][M]$$

Now what you do we use the steady state approximation for free radical A and B.

So, you find out the $\frac{d[A]}{dt}$ is:

$$\frac{d[A]}{dt} = 2K_1[A_2][M] - K_2[A][B_2] + K_3[B][A_2] - K_4[A][B][M]$$

For steady state, it goes to 0. Similarly,

$$\frac{d[B]}{dt} = K_2[A][B_2] - K_3[B][A_2] - K_4[A][B][M] = 0$$

So, if you get the simultaneous equation of 2.61 and 2.62 that is the above 2 equation we can find out for concentration of A. So that essentially solution of 2.61 and 2.62, so that will get us the concentration of A.

(Refer Slide Time: 22:05)

Which will be:

$$[A] = \frac{K_1}{2K_2}\frac{[M][A_2]}{[B_2]} + \frac{K_3}{K_4}\frac{[A_2]}{[M]}\left\{\left[1 + \left(\frac{K_1K_4}{2K_2K_3}\frac{[M]^2}{[B_2]}\right)^2\right]^{1/2} - 1\right\}$$

So, it involved algebra, so this is how simultaneous equation of these two equations. Similarly one can get one can find out for concentration of B, the steady state values of A and B so now you get the steady-state values of A and B, and we can find out:

$$\frac{d[A_2]}{dt}, \frac{d[B_2]}{dt}, \frac{d[AB]}{dt}$$

For some initial values of K_2 and B_2, so that is how for different reactions and using the steady state approximation for chain reaction one can find out the other thing.

(Refer Slide Time: 23:47)

Now if we considered the simplest of the tree that means if you consider $\frac{d[B_2]}{dt}$ it is nothing but:

$$\frac{d[B_2]}{dt} = -\frac{K_1}{2}[M][A_2] - + \frac{K_2 K_3}{K_4}\frac{[A_2][B_2]}{[M]}\left\{\left[1+\left(\frac{K_1 K_4}{2K_2 K_3}\frac{[M]^2}{[B_2]}\right)^2\right]^{1/2}-1\right\}$$

So the last two equations can be further simplified and one may write:

$$K_1 K_4 [M]^2 \Big/ (2K_2 K_3 [B_2]) \ll 1$$

(Refer Slide Time: 25:08)

So, if you do that then things K_2 and K_3 is larger than K_1 and K_4 for steady state approximation to apply. So, this is valid for steady state approximation to apply then from equation 2.63 and 2.64 one can approximate that is:

$$[A] \approx \frac{K_1}{2K_2}\frac{[M][A_2]}{[B_2]} + \frac{K_1^2 K_4}{8K_2^2 K_3}\frac{[M]^3[A_2]}{[B_2]^2}$$

So,

$$\frac{d[B_2]}{dt} \approx -\frac{K_1}{2}[A_2][M] - \frac{K_1^2 K_4}{4K_2 K_3}\frac{[M]^3[A_2]}{[B_2]}$$

So, in both the equations 2.65 and 2.66 first term which is this term and this term they actually dominates at low pressure situation. So, when you have a low pressure situation, these terms are actually dominating.

(Refer Slide Time: 27:03)

Now concentration of A one can look at that depends on the primarily in the ratio of k_1 and k_2 and rate at which B_2 disappears is also governed by k_1. Increasing k_2 and k_3 increases radial concentration, but it does not have any effect on production rate of the products. And concentration of A and B directly proportional to pressure and reaction rate for major species scales with pressure. So now provided the second term in this two equations that means this time and this term they are small.

2: Chemical kinetics

- At high pressures, the second terms in Eqns. 2.65 and 2.66 become important (they increase with pressure faster than the first terms do).
- So, k_4 has some influence at high pressures, although it does not have much influence on radical concentrations or overall reaction rate at lower pressures.
- *Chain-branching reactions* involve the formation of two radical species from a reaction that consumes only one radical.

$$O + H_2O \longrightarrow OH + OH$$

INDIAN INSTITUTE OF TECHNOLOGY KANPUR   Ashoke De 52

So, but at high pressure those two terms become quite important because they will increase the pressure then the first terms do. Therefore has some influence at high pressure but not the low pressure. So, when you look at these two expressions and try to find out the important So, k_4 has at high pressure it is important but at low pressure it is not and till then reactions in the formation of 2 radical species form a reaction that consume on radical.

For example like this:

$$O + H_2O \rightarrow OH + OH$$
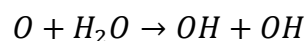
Ok? So now once you do this that means when you find out the steady state approximation using this change branch in reactions find out this concentration expression data dependency of the pressure and that will allow to see how that BF and then will find out the chemical terms gets calculation or will look at the chemical time scale calculation in the next lecture, we stop here today.