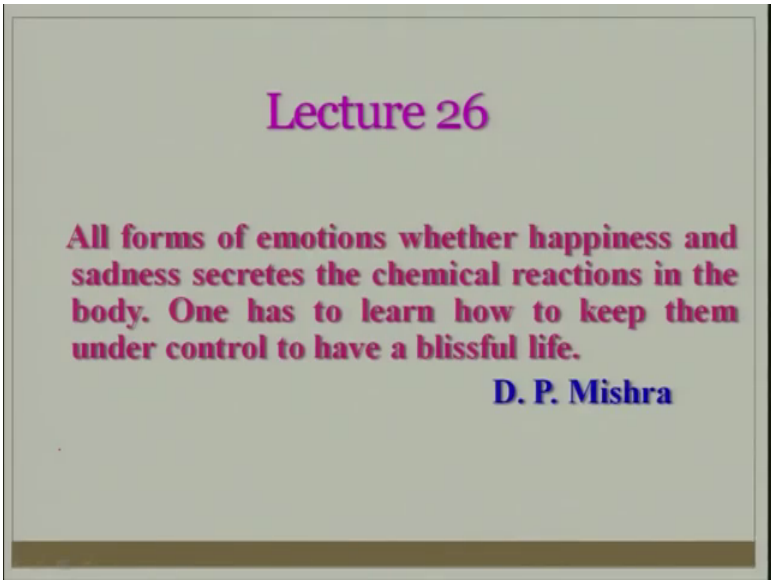
Fundamentals Of Combustion (Part 1)

Dr. D. P. Mishra
Department of Aerospace Engineering
Indian Institute of Technology, Kanpur

Lecture - 26
Classification of chemical reactions

Let us start this lecture with a thought process, all forms of emotions whether happiness and sadness secretes the chemical reactions basically hormones you know in the body.

(Refer Slide Time: 00:19)



Lecture 26

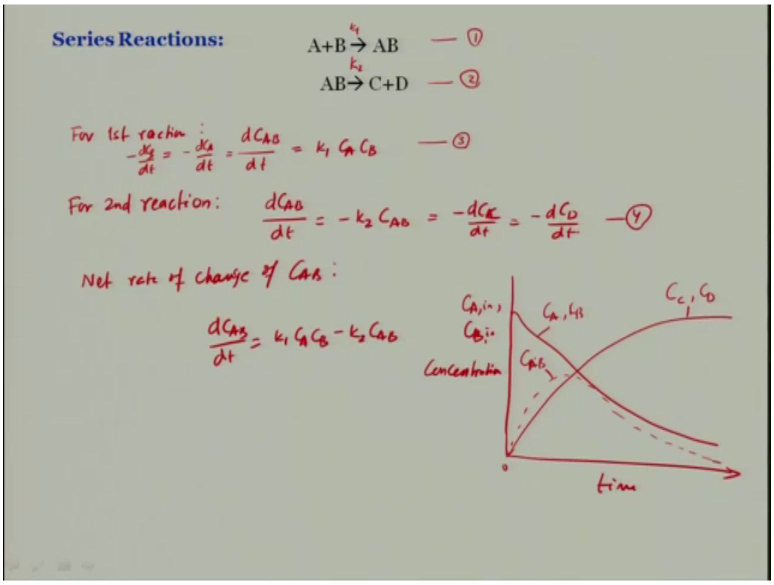
All forms of emotions whether happiness and sadness secretes the chemical reactions in the body. One has to learn how to keep them under control to have a blissful life.

D. P. Mishra

One has to learn how to keep them under control to have a blissful life because you will have to basically take care of secretion of your hormone through your mind. So, let us recall what we learnt in the last lecture.

In the last lecture basically we have discussed about first order reaction, second order reaction and third order reaction, right? Today what we will do? We will look at also different kinds of reactions, right? Little bit then we will move into elementary reactions, right?

(Refer Slide Time: 01:05)



Series Reactions:

$$A+B \xrightarrow{k_1} AB \quad — ①$$

$$AB \xrightarrow{k_2} C+D \quad — ②$$

For 1st reaction:

$$-\frac{dC_B}{dt} = -\frac{dC_A}{dt} = \frac{dC_{AB}}{dt} = k_1 C_A C_B \quad — ③$$

For 2nd reaction:

$$\frac{dC_{AB}}{dt} = -k_2 C_{AB} = -\frac{dC_C}{dt} = -\frac{dC_D}{dt} \quad — ④$$

Net rate of change of C_{AB}:

$$\frac{dC_{AB}}{dt} = k_1 C_A C_B - k_2 C_{AB}$$

So, let us first look at reaction in series, right? That means, the reaction will be occurring in series ways the way we do the relay, race relay race you know? One fellow will take one button and then give to other other will run you know that way. So, that is in series.

Let say A molecule is reacting with B getting into A B, right? And this A B is decomposed into C and D. If I say this is reaction 1 and this is reaction 2 let say this is k 1 and this is your basically rate coefficient or reaction rate coefficient or people call it also rate constant, right? So, for that for the first reaction, what would be the reaction rate? That is d C A B if I look at by dt; that means, how much of molecule A B is you know concentration changing with respect to time is equal to k 1 C A and C B, right? I can say this is basically 3 keep in mind that this is equal to.

What is that? D C A by dt, yes or no? That is equal to also minus d CV by d t because this is getting consumed, right? And for second reaction, I can write down in similar way dC A B by dt is equal to what minus k 2 C A B, right? And of course, that you can say also similar way minus d C A by dt sorry dc by dt is equal to minus d C D by dt. And that is equation 4 what will be considering now what is the net what you call production of C A B that we need to find out, right? You will find out the net rate of change of C A B would be d C A B by dt is equal to k 1 C A C B minus k 2 C A B, right?

Now, of course, if I know this rate coefficient and concentration of all these thing I can find out very easily, right? And if you look at this C A B at time is equal to 0, what it would be? It will be 0 because there is nothing C A B, right? In the beginning what are the molecules are there A and B, some initial concentration will be there, right? And C and concentration of C and D also will be 0 isn't it, yes or no?

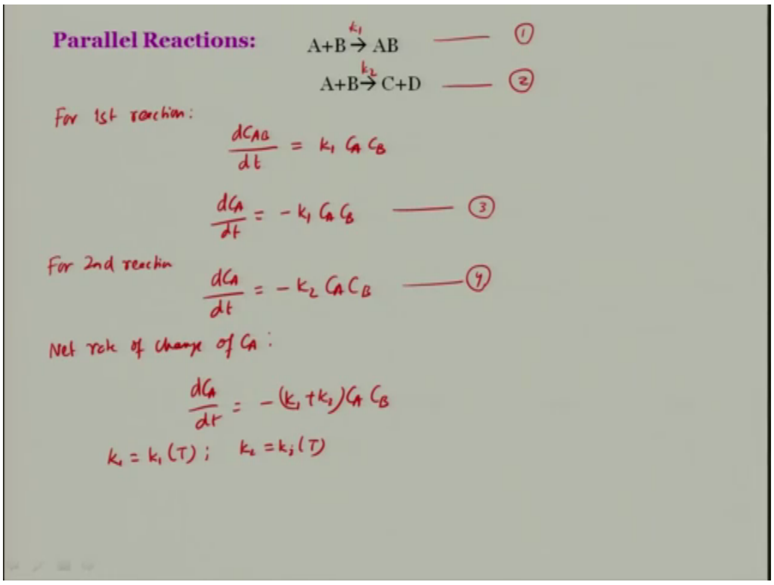
For example, if I will plot it with respect to time this is concentration, right? and in the beginning what will happen there will be A and B I can say this will be A B will be changing like this this is concentration of C A and C B of course, at this point t is equal to 0 what will be C A in and C A C B in keep in mind that this concentration need not to be same I have plotted here, but need not to be same, right? And there might be 2 plots you know you can say think of, but here I have just doing just a simplicity.

But my point is not that; like what will we at if you look at C C and C D it will be 0 to start with maybe it will be increasing, right? This is corresponding to C C and C D are you getting I just drawing it because I am assuming this concern a both have same C and B need not to be it will be different maybe, right?, But my point is not that my point is to say that; what will happen to the C A B, C A B in the beginning it will be 0 at the end of the reactions it may be 0 or maybe very small values ok.

In between what will be happening there might be a peak values, are you getting? There might be peak values this is your C A B. So, therefore, one has to really concern about how to handle this series reaction because it may be occurring in nature like in nature means when you were talking about multi step chemistry, right? You may need to look at that, right?

So, that is another way of also looking at the parallel reactions, right? So, we will be looking at parallel reactions, right?

(Refer Slide Time: 06:59)



Parallel Reactions: $A + B \xrightarrow{k_1} AB$ —— ①

$A + B \xrightarrow{k_2} C + D$ —— ②

For 1st reaction:

$$\frac{dC_{AB}}{dt} = k_1 C_A C_B$$

$$\frac{dC_A}{dt} = -k_1 C_A C_B$$ —— ③

For 2nd reaction

$$\frac{dC_A}{dt} = -k_2 C_A C_B$$ —— ④

Net rate of change of C_A:

$$\frac{dC_A}{dt} = -(k_1 + k_2) C_A C_B$$

$k_1 = k_1(T)$; $k_2 = k_2(T)$

Let say that a molecule is reacting with B going to the A B; right. I can say this reaction one and with a reaction rate coefficient or the reaction rate constant is k 1, A B parallely will be decomposing into C and D, right? I can say this is the reaction 2. Keep in mind that there in other example what we see in the series series reactions basically, A B is decomposing into C and D.

But here A B which is the initial you know reactants that is going to some other product, right? That is the difference parallel it is parallely going on like you might be knowing today people are doing parallel computing you know, right? So, if the reaction is going on parallely, a question might be coming to your mind when this reaction 1 will be predominant the reaction 2 will be predominant, is that question coming to your mind? There might be some situation where reaction A will be very vigorously occurring and B will be taking a backseat, right? Or there will be in in the same rate it is not really possible or maybe possible I do not know I mean maybe some range, right?

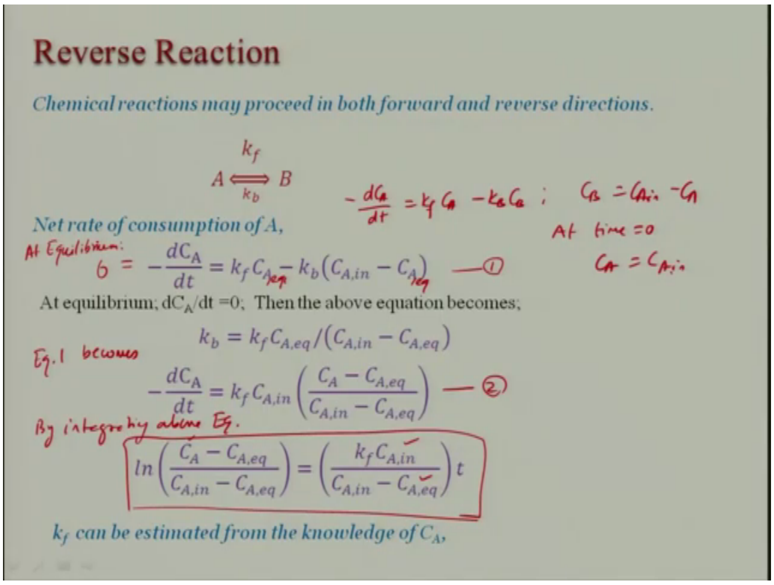
So, when it will be you think about it, I will discuss that little later on for first reaction I can write down C A B change in concentration of A B with respect to time is equal to k 1 C A and C B, but if I will be more interested to find out d C A by dt is equal to minus k 1 C A C B, isn't it, because this is getting consumed therefore, k 1 C. Now I can say this is the reaction 3 because I will be and for second reaction I can find out basically d C A by dt for the second reaction will be equal to minus k 2 C A C B, right?

Let say this is so net reaction net rate of change of or C A; right? Would be d C A by dt it will be minus k 1 plus k 2 C A C B, right? This simply just you add the equation 3 and 4 you will get, right? So that means, if you look at the reaction rate of molecule a, right? Will be basically dependent on the concentration A and concentration B and it will be dependent on also k 1 and k 2. Keep in mind that k 1 k 1 is a function of what we have already seen temperature k 1 is a function of temperature.

Similarly, k 2 is a function of also temperature, right? And for example, like at certain temperature k 1 may be very high; that means, that is which one predominant, right? And at certain temperature k 2 may be predominant. So, as a result if you look at that way you will have to take care of this parallel reaction which is important with a certain range; let say 500 kelvin you know certain reaction will be very important like the reaction 1 is important.

But in the let say something may be 1000 to the 2000 kelvin may be reaction 2 is important, right? Because that is giving you higher values depending on your activation energy, right; kind of thing. So, therefore, you need to learn how to handle this parallel reactions and then reaction in series or series reactions kind of things. And all these reaction what we have deal do it we are only considering the forward reaction rate we are not considering reverse reaction or the backward reaction let us see how we will handle that.

(Refer Slide Time: 12:09)



Reverse Reaction

Chemical reactions may proceed in both forward and reverse directions.

$$A \underset{k_b}{\overset{k_f}{\Longleftrightarrow}} B$$

$$-\frac{dC_A}{dt} = k_f C_A - k_b C_B \; ; \quad C_B = C_{A,in} - C_A$$

At time =0

$C_A = C_{A,in}$

Net rate of consumption of A,

At Equilibrium:

$$0 = -\frac{dC_A}{dt} = k_f C_{A_{eq}} - k_b(C_{A,in} - C_{A_{eq}}) \quad — ①$$

At equilibrium; $dC_A/dt = 0$; Then the above equation becomes;

$$k_b = k_f C_{A,eq}/(C_{A,in} - C_{A,eq})$$

Eq. 1 becomes

$$-\frac{dC_A}{dt} = k_f C_{A,in}\left(\frac{C_A - C_{A,eq}}{C_{A,in} - C_{A,eq}}\right) \quad — ②$$

By integrating above Eq.

$$\boxed{ln\left(\frac{C_A - C_{A,eq}}{C_{A,in} - C_{A,eq}}\right) = \left(\frac{k_f C_{A,in}}{C_{A,in} - C_{A,eq}}\right)t}$$

k_f can be estimated from the knowledge of C_A,

So, reverse reaction if you look at I am just considering you know like because of fact that the chemical reaction may proceed in both forward and reverse direction, right? Of course, keep in mind that I had also discuss showing some data that the activation energy pre-exponential factors and temperature coefficients need not to be same; that means, reaction rate will be different it need not it would not be same. Let say a is reacting you know and going to the product B with what you call reaction rate coefficient k f and when B is coming back to the a that is k b, right?

So, net reaction rate of congestion of A will be basically k f and C A, right? And what will be if you look at if I write down this equation this will basically dt is equal to k f C A minus k b C B, right? And what I am saying C B is nothing but C A initial minus C A whatever being consumed that is nothing but your C B, right? That means, this is with respect to time at any instant C A and this is initial the difference will be basically nothing but C B keep in mind that this is true only for the simple reaction what I have considered this need not to be true for if it is a bimolecular reactions kind of thing, right?

Now, so what will do now I will assume the equilibrium, right? Generally what is being done you reverse reaction you know rate need not to be there, but you can find out by assuming it to be equilibrium, right? They do that. Then above with for simplicity reason and then above equation becomes, right? Kb is equal to kf C A equilibrium, right? Because when I am saying this is 0, right? This is 0 then I am saying this is equilibrium, right? And this is also in equilibrium, right when this is 0 at equilibrium.

So, naturally what will be kb kb is equal to kf C A equilibrium divided by C A initial; that means, this is C A is basically at time is equal to 0 C A is C A initial, right? So, C A initial minus C equal; that means, you can get this reverse reaction rate coefficient in terms of forward reaction rate coefficient and of course, you know the initial values of concentration, you know the equilibrium values of molecule a then only you can find out very easily. And this is the standard procedure what is being used because of simple sitted region, right?

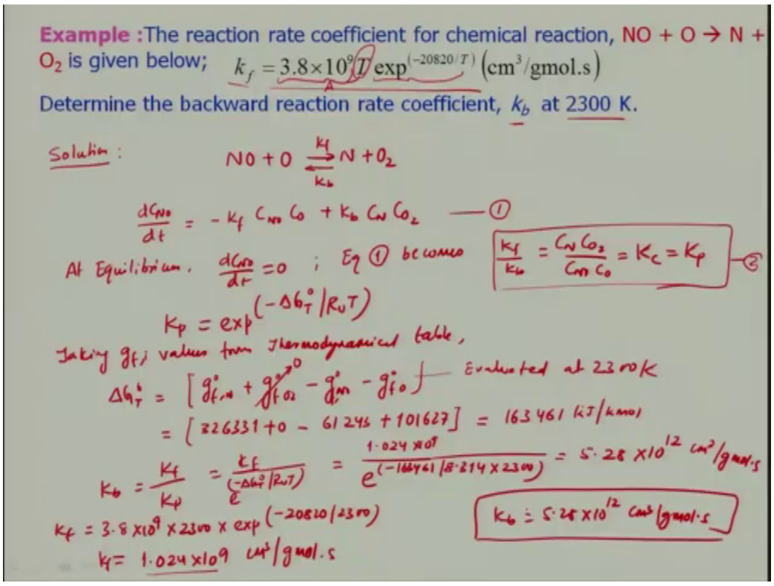
And then I can write down basically if I say this is equation one and equation 1 becomes like d C A by dt nothing, but k f C A initial, right? And C A minus C A equilibrium divide by C A in minus C A equilibrium, right? That means, if you look at, right? I mean I can avoid this C V, right? Because I have already in place of cv I have put it here in this and then I am getting C V is relationship.

So, if I will integrate this by integrating above equation like and say 2 I can get this D C A minus C A equilibrium divide by C A in minus C A equilibrium kf C A in divide by C A in see well as there will be some constant and you will have to evaluate you know C at the initial t is equal to 0 that will go away and then you will get final result, right?

So, this will be basically final result what you will get. You can do that and then find if you will find difficulties we will see how you can. So, by that what will happen I can also by knowing this kf, right? I can handle, right? Because I can find out what is the how the C A is varying with, right? Keep in mind that here we are taking the at equilibrium d C A by dt is 0; that means, you know that is the equilibrium condition we are considering for the calculating the backward reactions, right?

So, if I look at this way like I can if I know the C A, right? If I know the concentration C A I can also find out what is the kf because all are known this equilibrium will be known this will be known, right? And if I measure this C A at certain time, right? Then I can find out what is the k f, right? Even if I do not know that k for this simple thing.

(Refer Slide Time: 18:03)



Example : The reaction rate coefficient for chemical reaction, NO + O → N + O_2 is given below; $k_f = 3.8\times10^9\,T\,\exp^{(-20820/T)}\,(\mathrm{cm^3/gmol.s})$

Determine the backward reaction rate coefficient, k_b at 2300 K.

Solution :

$$NO + O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} N + O_2$$

$$\frac{dC_{NO}}{dt} = -k_f C_{NO} C_O + k_b C_N C_{O_2} \quad — ①$$

At Equilibrium, $\frac{dC_{NO}}{dt} = 0$; Eq ① becomes $\boxed{\frac{k_f}{k_b} = \frac{C_N C_{O_2}}{C_{NO} C_O} = K_c = K_p}$ — ②

$$K_p = \exp^{(-\Delta G_T^0/R_u T)}$$

Taking $g_{f,i}$ values from Thermodynamical table,

$$\Delta G_T^0 = [g^0_{f,N} + \cancel{g^0_{f,O_2}}^{0} - g^0_{f,NO} - g^0_{f,O}] \quad \text{— Evaluated at 2300 K}$$

$$= [226331 + 0 - 61246 + 101627] = 163461\ \mathrm{kJ/kmol}$$

$$k_b = \frac{k_f}{K_p} = \frac{k_f}{e^{(-\Delta G_T^0/R_u T)}} = \frac{1.024\times10^9}{e^{(-163461/8.314\times2300)}} = 5.28\times10^{12}\ \mathrm{cm^3/gmol.s}$$

$$k_f = 3.8\times10^9 \times 2300 \times \exp^{(-20820/2300)}$$

$$k_f = 1.024\times10^9\ \mathrm{cm^3/gmol.s}$$

$$\boxed{k_b \doteq 5.28\times10^{12}\ \mathrm{cm^3/gmol.s}}$$

So, let us take an example like you know how to determine the backward reaction rate coefficient, right? So, this example is reaction rate coefficient for chemical reaction NO plus O going to the N plus O O 2, right? And the the reaction rate coefficient is given by this kf like it is if you look at this is your pre-exponential factor this portion, right, right? And this is of course, this is temperature coefficient in this case B in our this thing is equal to 1, right? T and this is your exponential factor, right? And keep in mind this is centimeter cube per gram mole second and we will have to determine the backward reaction rate coefficient k B at 200 2300 Kelvin, right? 2300 kelvin.

So, what we will have to do for this? What we will have to do? Because we know the the chemical reaction is given, right? This is a very famous reaction, right? N plus O 2, right? And this can take place in the both the direction, right? I can say kf and in the backward direction this is kb. So, I can write down the concentration of the N O or the reaction rate of N O no by dt is equal to minus kf C N O C O plus kb C N C O 2 isn't it, right? And for that what we will do we will basically look at at equilibrium what is happening like at equilibrium N O dt is 0, right?

If that is 0 if I say this is equation then equation one becomes, right? K f by k B is nothing but C N C O 2 by C N N O co and keep in mind that this is nothing but your what kc, right? Can I say this is equal to kp equilibrium m constant this is big capital I am writing because by molecular reaction. So, therefore, the pressure by this term R u T it would not be coming ok. So, therefore, it is possible only one and keep in mind that kp is a non-dimensional parameter, right? And what is that kp, kp we know is nothing but exponential delta G T naught divided by R u T, right?

Now I will have to evaluate this one, right? Delta G naught for that data is to be given and taking data g f I values, right? from thermo dynamical table, right? I have already shown you table it is there on the backside of textbook also. So, you can find out delta G T naught is equal to g f n naught plus g f O 2 naught, right? Minus g N O f naught minus g f o naught. Now of course, is it true because all are these things? So, that is fine so this O 2 if you look at O 2 will be 0, right? If I will substitute these values, right? There data's of gf n and gf N O and gf o I will be taking from the thermodynamic table corresponding to what temperature.

Student: 23.

2300 kelvin, right? At right? So, I will just put these values here because I am not getting to table, but you will have to do our given table go to table and solve 6 3 1 plus 0 minus

6 1 2 4 3 plus 1 0 1 6 2 7 is equal to 1 6 3 4 6 one kilo joule per kilo mole. Keep in mind these are evaluated these values are evaluated, right? at 200 Kelvin, right?.

Now, if you look at this kp values I can evaluate very easily. And then from this expression if I say this is equation 2 I I am I am interested to find out kb. So, kb will be nothing but your kf into kp yes or no? And kf is given to you, right? So, and kp you can evaluate because you know this thing so let me write down here that is, e delta G T R u T minus, right? Are you you know T is not, but I will have to find out basically k f. Kf I know is very easily I can find out from this expression is given 3.8 10 power till 9 into 2300 for this temperature into exponential of 2 0 8 2 0 2 3 0 0. And this happens to be k f I am getting one point 0 2 4 10 power till 9-centimeter cube gram mol second.

So, if I will put these values here, right? 1.024 into 10 power to till 9, right? E this is 1 6 3 4 6 1 divided by 8.314 into 2300 if we will substitute this value you will get, right? Something 5.28 into 10 power 12-centimeter cube, right? Gram mol second. So, this is my kb values, right? 5.2810 power 12 centimeter cube gram mol second.

So, if you look at your kf is 10 power to 9, where as kb is 10 power to 12 you know like of course, there is a 5 also coming into picture. So, it is a reverse reaction is what you call having higher reaction rate coefficient, right? So, by this way you can really evaluate the reverse reaction. Keep in mind that we are taking that equilibrium as a condition like it is attaining equilibrium then only.

So, with this we will stop over. And we will discuss about what you call elementary reactions further in the next lecture.

Thank you very much.