Rate Processes

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Module No. #01

Lecture No. #05

Complex Reaction

Hello, very good morning to all of you, so today is the fifth lecture of rate processes.

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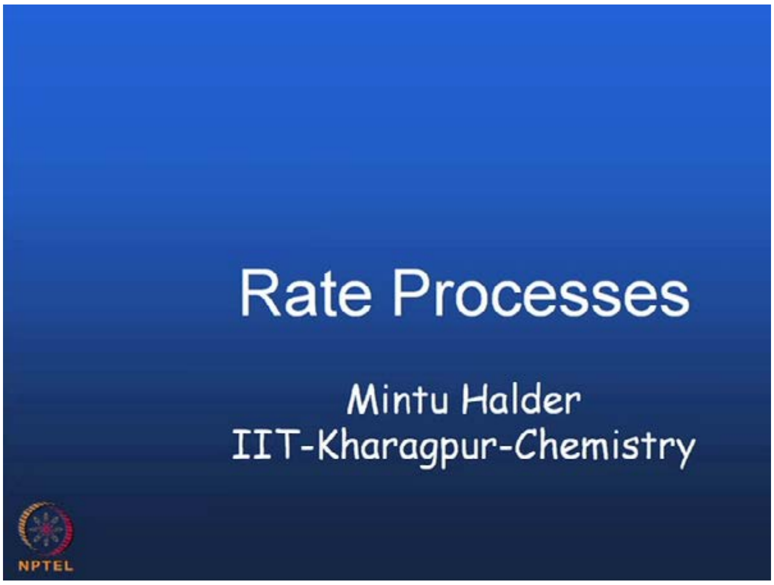

Rate Processes

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So, we completed two aspects, one is reaction rates and rate laws, next we completed effect of temperature on reaction rate.

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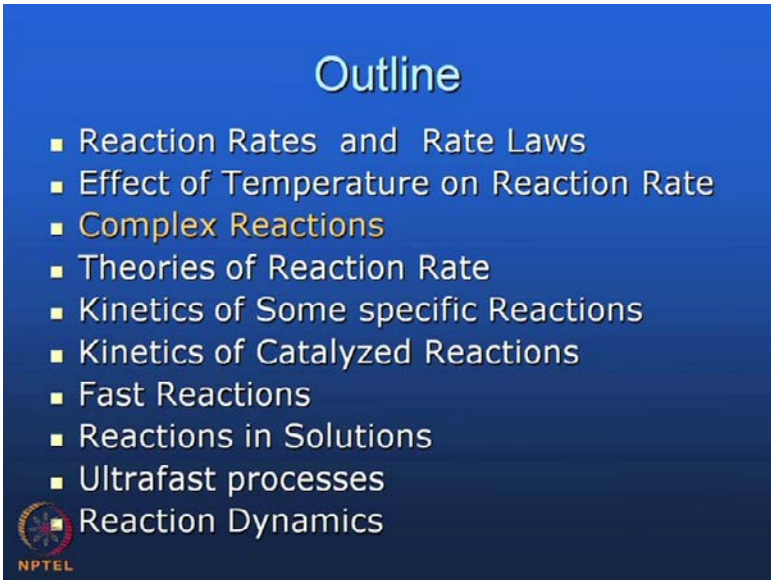

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

So, today we will focus on complex reactions. So before going into the details of this thing what is meant by a complex reaction, we will try to learn first and then we will move on to various types of complex reactions.

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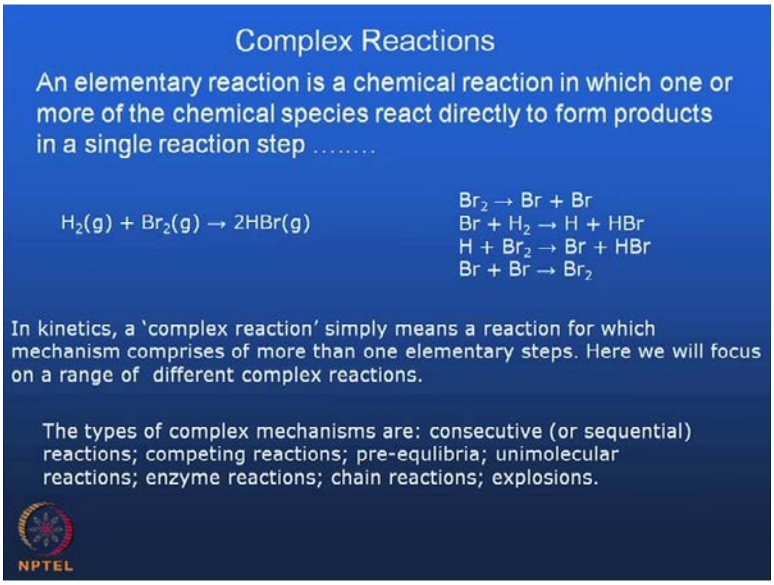

Complex Reactions

An elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step ……..

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$Br_2 \rightarrow Br + Br$
$Br + H_2 \rightarrow H + HBr$
$H + Br_2 \rightarrow Br + HBr$
$Br + Br \rightarrow Br_2$

In kinetics, a 'complex reaction' simply means a reaction for which mechanism comprises of more than one elementary steps. Here we will focus on a range of different complex reactions.

The types of complex mechanisms are: consecutive (or sequential) reactions; competing reactions; pre-equlibria; unimolecular reactions; enzyme reactions; chain reactions; explosions.

Now, an elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step. So, that is basically you know a total chemical reaction may be you must have divided into small a smaller type of you know chemical reactions.

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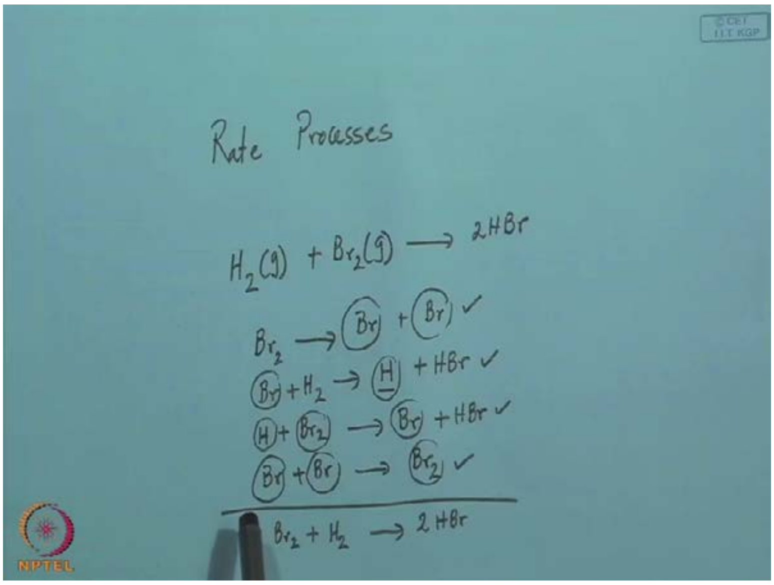

Rate Processes

$H_2(g) + Br_2(g) \longrightarrow 2HBr$

$Br_2 \longrightarrow Br + Br$ ✓

$Br + H_2 \rightarrow H + HBr$ ✓

$H + Br_2 \longrightarrow Br + HBr$ ✓

$Br + Br \longrightarrow Br_2$ ✓

$Br_2 + H_2 \longrightarrow 2HBr$

As per example if we concentrate on to this reaction like H 2 gas plus B r 2 gas, it is a gas phase reaction to produce twice H B r. So, this reaction has got a mechanism, which is known, which has been established by by various other means, which are known to follow you know the following steps. That is first B r 2 undergoes hemolytic cleavage to produce two bromine radicals or bromine atom, then one of these two bromine atoms then will react with dihydrogen that is H 2 to produce one hydrogen atom and a H B r. Then this hydrogen again will react with B r 2 to produce B r and another hydrogen bromide and then this B r again will react with B r to produce B r 2.

So, these are elementary reactions, so there are four elementary steps for this reaction, this is the net reaction. You see this is the net reaction, if you add, if you add this total then you will be getting, so this two will cancel over here and then these two will cancel. So, in this way, I mean you know and you see that there is on bromine that is this these two are cancelled, then this bromine and that bromine will cancel. So, to give you B r 2 plus H 2 producing twice H B r, so how this you know reaction mechanism is established, this part I will I will discuss in detail may be in some other you know lecture, but just to show you that you know a complex reaction, this is a complex reaction, so this complex reaction consists of four elementary steps. So, so an elementary reaction is a, this is a this is this is elementary reaction, so an elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step; this is a single reaction step.

So, in kinetics a complex reaction, simply means a reaction for which mechanism comprises of more than one elementary step, that means if it is a complex reaction at least two of of such elementary. So, such means like, may be at least two elementary reaction steps will be there and here we we will focus on a range of different complex reactions. So, basically you know if there are more than one elementary step we can call that reaction to be a complex reaction that is that the reaction is not a simple reaction, it's mechanism is not simple. The types of complex mechanisms are like consecutive reactions or it is also called as sequential reaction, then competing reacting, that is one reaction is competing with another, consecutive means A is giving rise to B and then B is giving rise to C. So, consecutive, that is sequential A to B to C, that is a sequential process, another situation is a pre-equilibria.

Next, it can be unimolecular reaction, so I will come to the point what is meant by molecularity, it is a different, it is bit different from the concept of order, because order is an experimentally derived quantity and molecularity is a theoretical concept that is based on on number of species involved in an elementary step. So, in this case it says, you see there are two species, two bromine atoms. So, it it is basically you know bimolecular, I mean diatomic you can say or may be here, like H 2 and B r, it is a bimolecular process. So, unimolecular, bimolecular, like unimolecular reaction is a complex reaction, then as I gave you some idea in earlier classes that enzyme reaction it is also not a simple reaction, it is also a complex reaction.

Then chain reaction, chain reaction means like you know this radical reactions or polymerization reactions, so these are you know chain reactions. So, chain reactions are also you know complicated, that is complex reaction.

Explosion as I told you that with increase of temperature, after certain temperature or above certain temperature there is a huge increase in rate, so explosion. Explosion is also, also a complex, is a case complex reaction, consecutive competing pre-equilibria unimolecular reactions, enzyme reactions, chain reactions, explosions; these are you know primarily complex you know reactions.

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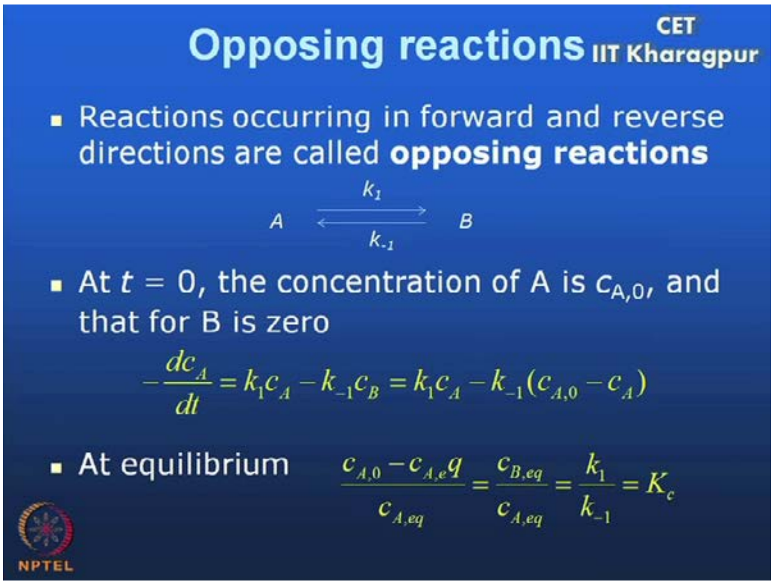

Opposing reactions

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- Reactions occurring in forward and reverse directions are called **opposing reactions**

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

- At $t = 0$, the concentration of A is $c_{A,0}$, and that for B is zero

$$-\frac{dc_A}{dt} = k_1 c_A - k_{-1} c_B = k_1 c_A - k_{-1}(c_{A,0} - c_A)$$

- At equilibrium $$\frac{c_{A,0} - c_{A,e}q}{c_{A,eq}} = \frac{c_{B,eq}}{c_{A,eq}} = \frac{k_1}{k_{-1}} = K_c$$

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So, first let us talk about this opposing reaction, it is also not a simple reaction you see, so it is occurring as I already told you, in may be some some other lecture, that equilibrium, so equilibrium and reaction. So, equilibrium is always there, if the equilibrium is far shifted towards the right then it is called that reaction is completed in the right hand direction. May be the back reaction is very small, but basically all reactions, for all reaction you can think of a back reaction. And if the back reaction is appreciable then this back reaction competes with the forward reaction and ultimately at certain point of time you may get equilibrium. So, reactions occurring in forward and reverse directions are called, means this are simultaneously occurring, are called opposing reaction, you see A to B.

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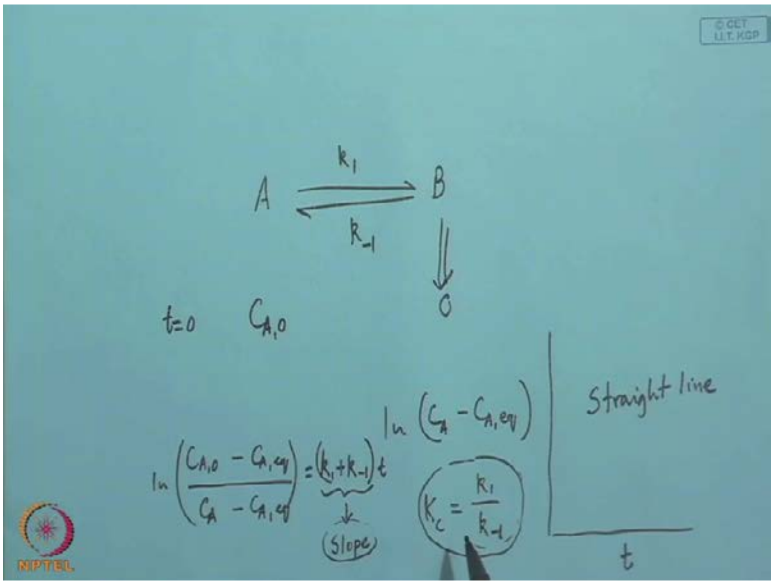

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$t=0 \quad C_{A,0} \quad 0$

$$\ln\left(\frac{C_{A,0} - C_{A,eq}}{C_A - C_{A,eq}}\right) = \underbrace{(k_1+k_{-1})}_{\text{Slope}} t$$

$$\boxed{K_c = \frac{k_1}{k_{-1}}}$$

So, forward rate constant is k 1, reverse rate constant is k minus 1, so when reaction has just started that is at t equal to 0, the concentration of A is C A 0, C A 0, 0 means at t equal to 0. And at t equal to 0 the concentration of B will be 0, because it has not been formed, it is yet to be formed out of A, so rate of disappearance of A can be written in this way. You can look into the slide that d C A d t is this k 1 C A minus k minus 1 C B, because this is the concentration of B, this is the concentration of A and so you can you can write in this way that k minus C A minus k minus 1 C A 0 minus C A. So, at equilibrium what we get, basically C A 0 minus C A, this is q is bigger, actually this will be e q, small like this. So, this you can write at equilibrium, you will be getting C B equilibrium by C A equilibrium is equal to k 1 by k minus 1, which is nothing but equal to concentration equilibrium constant k c.

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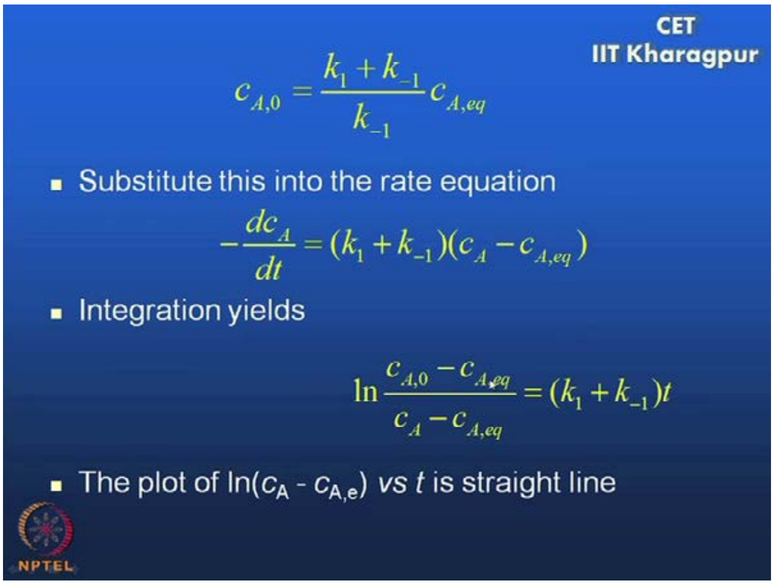

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$$c_{A,0} = \frac{k_1 + k_{-1}}{k_{-1}} c_{A,eq}$$

- Substitute this into the rate equation

$$-\frac{dc_A}{dt} = (k_1 + k_{-1})(c_A - c_{A,eq})$$

- Integration yields

$$\ln \frac{c_{A,0} - c_{A,eq}}{c_A - c_{A,eq}} = (k_1 + k_{-1})t$$

- The plot of ln(c_A - $c_{A,e}$) *vs t* is straight line

Then from this, from this you can get C A 0 is equal to k 1 plus k minus 1 by k minus 1, C A equilibrium and then substitute this into the rate equation, what was the rate equation? Rate equation was this. So, if you substitute this into the rate equation here, this one if you substitute this the expression for C, that is if you replace C A 0 in terms of C A equilibrium, that is the equilibrium concentration of A, then you will be getting this expression. d C A d t is with a negative sign is equal to k 1 plus k minus 1 times C A minus C A equilibrium, that is this is the concentration of A at equilibrium.

When the backward and the forward react, when these two are equalized upon integration we get this, upon integration we get this. Now, if we plot, if we plot because this is a you know C A 0 minus C A equilibrium, so equilibrium concentration has got some number, you know this is the starting concentration, this is the variable. So, if you plot l n C A minus C A equilibrium, e means equilibrium, this is equilibrium versus t, you will be getting plot of l n C A minus C A equilibrium. If you plot this versus t, you will be getting a straight line; you will be getting a straight line. So, from this straight line what do we expect? So, you see your expression is l n C A 0 minus C A equilibrium divided by C A minus C A equilibrium is equal to k 1 plus k minus 1 into t.

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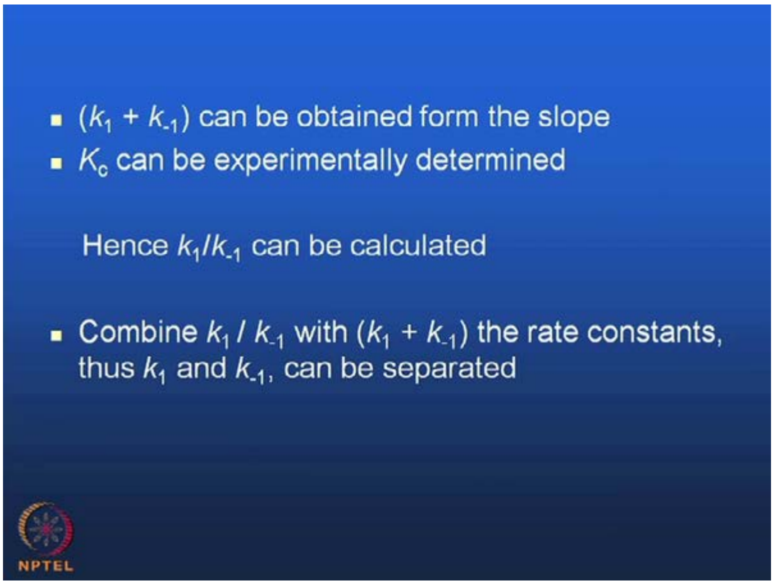

- $(k_1 + k_{-1})$ can be obtained form the slope
- K_c can be experimentally determined

Hence k_1/k_{-1} can be calculated

- Combine k_1 / k_{-1} with $(k_1 + k_{-1})$ the rate constants, thus k_1 and k_{-1}, can be separated

So, this is your slope, this is your slope, so slope you will be getting, you will be getting, I mean from this plot, so this is your slope, so from this plot you will be getting k 1 plus k minus 1 and your equilibrium constant, equilibrium constant that is k C can be determined experimentally. Experimentally means, equilibrium constant there are various ways of finding out the equilibrium constant, so k C is equal to k 1 by k minus 1 that can be experimentally calculated or obtained. So, if you now combine this slope and this we will be separating out k 1 and k minus 1, that means we can find out k 1 and k minus 1.

So, what is the prescription? Prescription is that l n C A, so it is, this is a, this is an opposing reaction, so this is an opposing reaction with forward rate k 1 with A backward rate or reverse rate k minus 1 and then we will plot, what we will do, experimental we will have an experimental plot that l n C A minus C A equilibrium versus time. We plot this, we will be getting a straight line, from this straight line we will be getting the slope which is nothing but, equal to k 1 plus k minus 1 and equilibrium experiments will be giving you, will be giving you the k 1 by k minus 1 number. So, from this two you will be able to find out the forward rate and the backward or the reverse rate.

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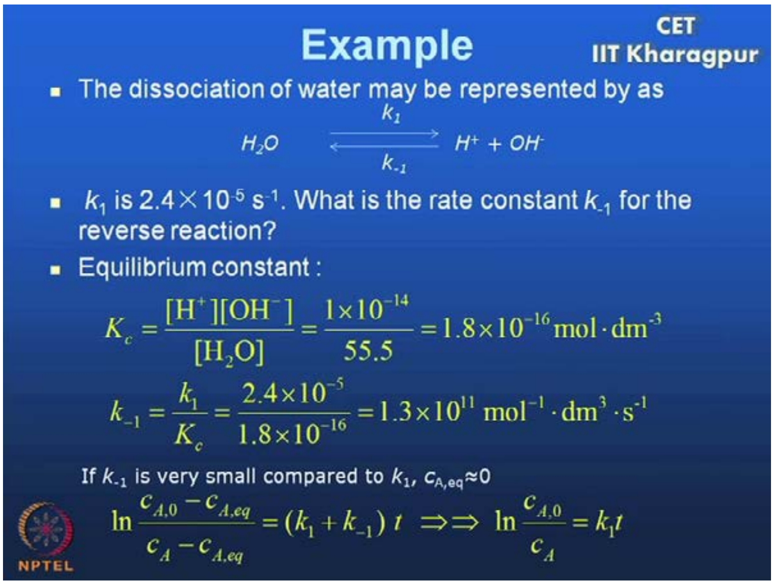

Example

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- The dissociation of water may be represented by as

$$H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + OH^-$$

- k_1 is 2.4×10^{-5} s^{-1}. What is the rate constant k_{-1} for the reverse reaction?
- Equilibrium constant :

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} = \frac{1\times10^{-14}}{55.5} = 1.8\times10^{-16}\,mol\cdot dm^{-3}$$

$$k_{-1} = \frac{k_1}{K_c} = \frac{2.4\times10^{-5}}{1.8\times10^{-16}} = 1.3\times10^{11}\,mol^{-1}\cdot dm^{3}\cdot s^{-1}$$

If k_{-1} is very small compared to k_1, $c_{A,eq}\approx 0$

$$\ln\frac{c_{A,0}-c_{A,eq}}{c_A-c_{A,eq}} = (k_1+k_{-1})\,t \Rightarrow\Rightarrow \ln\frac{c_{A,0}}{c_A} = k_1 t$$

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Let’s have an example that disassociation of water.

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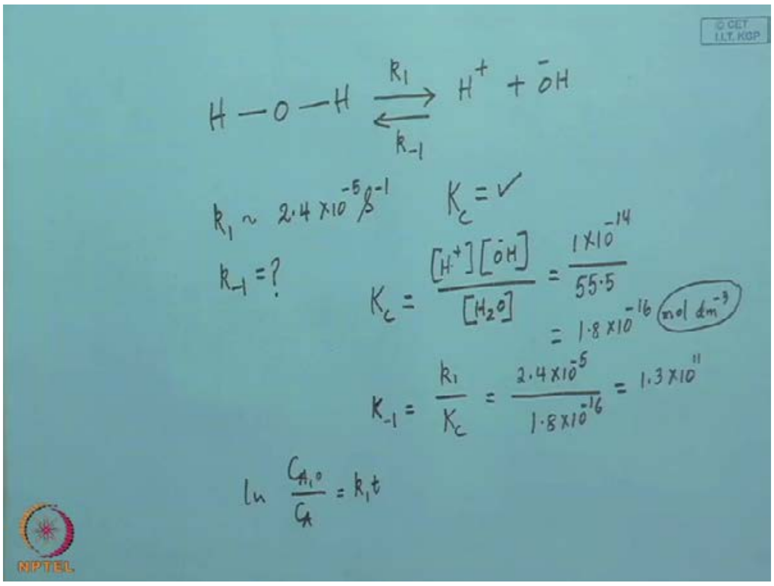

$$H-O-H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + \bar{O}H$$

$k_1 \sim 2.4\times10^{-5}\,s^{-1}$ $\quad K_c = \checkmark$

$k_{-1} = ?$

$$K_c = \frac{[H^+][\bar{O}H]}{[H_2O]} = \frac{1\times10^{-14}}{55.5}$$

$$= 1.8\times10^{-16}\ \text{mol dm}^{-3}$$

$$K_{-1} = \frac{k_1}{K_c} = \frac{2.4\times10^{-5}}{1.8\times10^{-16}} = 1.3\times10^{11}$$

$$\ln\frac{C_{A,0}}{C_A} = k_1 t$$

So, water, you know it is H o H, so it dissociates heterolytically to give you H plus and o H minus. So, with the forward rate k 1, reverse rate k minus 1, so k 1 is known to be k 1 is known to be of the order of 2.4 into 10 to the power minus 5 second inverse, per second this much and you would like to find out k minus 1 is equal to how much, so what to do? How to find out k minus one? So, as I told you in last slide that the prescription is that we should know the equilibrium constant k C that is the concentration equilibrium constant, it should be known and we have got this one. So, from this we should be able to find out k minus 1, so k C is equal to H plus concentration divided by o H minus concentration, I mean into o H minus concentration divided by water concentration.

So, this says, this H plus o H minus if you recall p H, I mean I the product of water, then this will be 1 into 10 to the power minus 14 at may be 25 degree centigrade and water is the concentration in molar concentration 55.5 molar. So, this gives you 1.8 into 10 to the power minus 16 mol, I mean, mol per decimeter cube means equilibrium, it is basically equilibrium constant should not have any unit, but it is just to show that it is it is when you know expressed in mol per decimeter cube. So, mol d m to the power minus 3, so it is not the unit the of you know a thermodynamic equilibrium constant, because thermodynamic equilibrium constant does not have any unit, but this is just to remember that it is mol per decimeter cube.

So, you know k minus 1, k minus 1 will be equal to k 1 by k C, which is equal to 2.4 into 10 to the power minus 5 divided by 1.8 into 10 to the power minus 16, which is equal to back reaction. So, 1.3 into 10 to the power 11, it is a back reaction, so it has got this this huge number, it has got this huge number, so that means you know is if you think that it is a tremendous back reaction, you see it is 10 to the power 11. Back reaction is at the order of you know 10 to the power 11 and the forward reaction is 10 to the power minus 5, so it is a very favourably ionized, it is mostly in water form, mostly in water form.

So, you know it is predominantly, you know back reaction is predominant than the forward reaction, so in this, in this particular discussion just do not you know consider these units, this is just to remember that in which unit these things are expressed. And here also also you get the appropriate unit from this mathematical expression, because it is a dimensionless quantity, so it is having a dimension per second, so that means it will also have per second kind of thing. So, anyway and also in the in this case one more important point is that, so these units you should not recall from here, means from here you should get the actual kinetic expression and from that you try to device, you try to find out what should be the unit for this minus 1.

So, it is for your you know practice, you can try. So, basically you do not use this dimensions over here, you try to find out by your own dimensions and also try to check whether these dimensions are ok or not, when you finding that this k C should not have any unit anyway. Now, if you know if k minus 1 is very small here, in this case, for this reaction k minus 1 is huge huge compared to k 1, so if this is very small compared to the forward reaction then then C A equilibrium will be very close to, that is C A equilibrium, this one will be, I mean left hand will be very close to 0 and your expression, your expression will get simplified into into this l n C A 0 by C A is equal to k 1 into t, ok.

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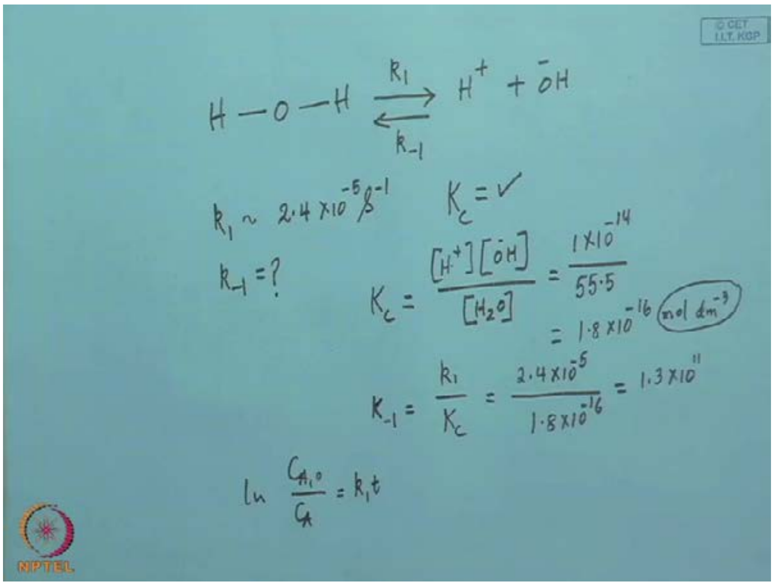

$$H-O-H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + \bar{O}H$$

$k_1 \sim 2.4 \times 10^{-5}\, s^{-1}$ $K_c = \checkmark$

$k_{-1} = ?$

$$K_c = \frac{[H^+][\bar{O}H]}{[H_2O]} = \frac{1 \times 10^{-14}}{55.5}$$

$$= 1.8 \times 10^{-16}\ \boxed{mol\ dm^{-3}}$$

$$K_{-1} = \frac{k_1}{K_c} = \frac{2.4 \times 10^{-5}}{1.8 \times 10^{-16}} = 1.3 \times 10^{11}$$

$$\ln \frac{C_{A,0}}{C_A} = k_1 t$$

Let’s move on to the next slide, that parallel reaction. So, what is a parallel reaction? Parallel reaction means reaction you know may be a substance which is undergoing a reaction to give you B, say A is giving you B, A is giving you B and maybe there is A possibility that the same substance is also undergoing another process, that is A parallel process, that is not giving you b, but it is giving you C. So, that means, this reactant A has got parallel reactions, has got parallel reactions like with a rate forward rate of k 1 giving you B and with a another forward rate k 2 giving you C. So, that means, A is giving you, it is it is also called a competing reaction, that is they are competing. And whether this particular step will be predominating or this particular step will be predominating that is determined by you know this rate constants, that is k 1 and k 2, whether this will be predominating or that will be predominating. So, grossly these two are almost close to each other, then both will be happening almost with equal probability, but if there is a difference in magnitude of k 1 and k 2, then the situation will be different.

So, rate of formation of B, that is d C B d t is equal to k 1 into C A, so formation rate will be k 1 into C A and also this C A rate of formation of C d C c d t is k 2 C A. So, the overall rate of, so basically we are writing in terms of product formation, so if you talk in terms of A, because A has got two channels, one is this channel, another is this channel. So, overall reaction, I mean, overall disappearance of A, that is minus d C A d t is equal to d C B d t plus d C c d t, because it is a sum of these two, you know sum of these two rates. So, if you write, then it is written like k 1 C A k 2 C A, that is k 1 plus k 2 into C A, so overall reaction, an overall reaction means it is basically, we initially assume that this a first order kinetics. So, overall reaction, overall disappearance of A is the sum of the individual disappearances, that is why k 1 plus k 2 is coming here as the overall k. So, overall k will be the sum of the individual first order case.

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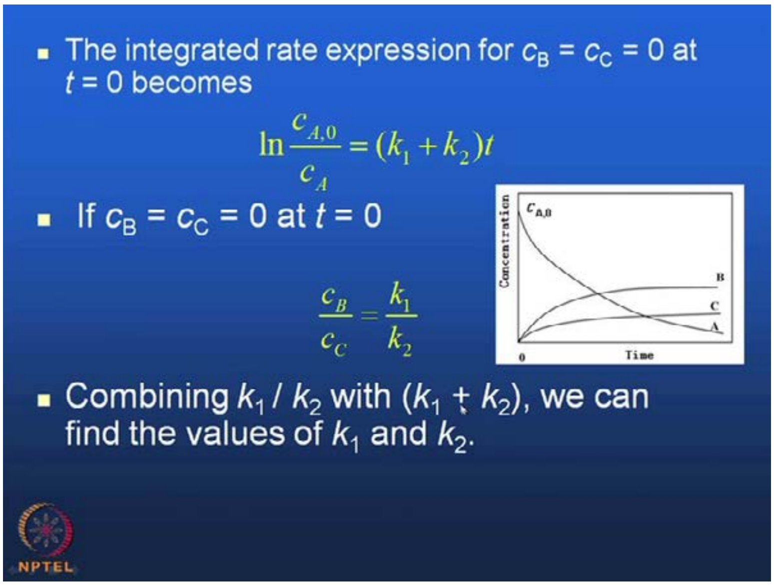

- The integrated rate expression for $c_B = c_C = 0$ at $t = 0$ becomes

$$\ln\frac{c_{A,0}}{c_A} = (k_1 + k_2)t$$

- If $c_B = c_C = 0$ at $t = 0$

$$\frac{c_B}{c_C} = \frac{k_1}{k_2}$$

- Combining k_1 / k_2 with $(k_1 + k_2)$, we can find the values of k_1 and k_2.

So, the integrated rate expression, so if you integrate this one, if you integrate this one, so integrated rate expression will be like, will be at t equal to 0, at t equal to 0 C B and C C, these are 0. So, if you integrate you will be getting this expression, that is l n C A 0 that is you know this is A, this is your initial concentration at t equal to 0, is equal to k 1 plus k 2 into 2 t. So, this is basically you know A like a first order, you see l n A 0 by A is equal to k into t, only difference is that, it is a sum of the individual case, k values. Sum of the individual k value that this happen only because of the fact that both steps elementary, you know it is a it is like elementary step, so both steps are first order. So, you know and if we plot then will be say it is like this, C A 0 it is the starting concentration, it is depleting to give you sum A. So, A is reducing with time and B and C these two are exponentially rising, whether this will be produced in larger proportion or this will be produced in larger proportion, that is decided by, that is decided by the their their relative you know rate constants, that is the magnitude of k 1 and k 2.

So, you can, you know if you want to find out C B by C C, that is this one C B by C C, so concentration of B by concentration of C, then it will be related by you know k 1 by k 2. So, combining k 1 by k 2 and k 1 plus k 2, k 1 by k 2 means this is basically what? Combining k 1 by k 2 means this is concentrational equilibrium, concentration of B by C, may be you can think in that way. So, combining k 1 by k 2, this one, with k 1 plus k 2, because k 1 plus k 2 will be getting from this plot, l n 1 by C A versus t you will be getting a straight line and from the slope you will be getting k 1 plus k 2, so if you combine k 1 by k 2 with k 1 plus k 2 you can find the individual values of k 1 and k 2. So, the point is that it is also acting like a first order decay, only difference is that that this is decaying in two parallel channels, two parallel channels channels B and C, ok.

Now, if you think of temperature what will happen? Now, as I told you in earlier lectures like that high temperature is favourable to the reaction with a large activation energy, that is the reaction which is having very high activation energy, that reaction will be favoured if the temperature is increased.

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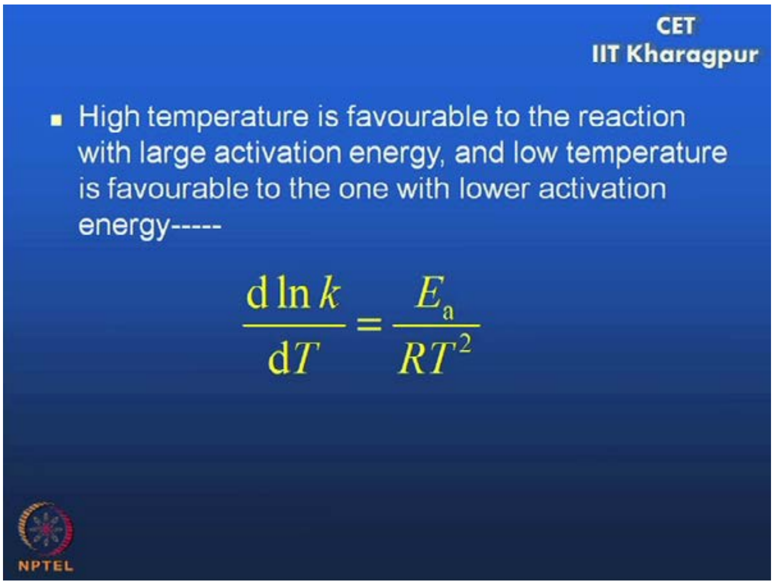

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- High temperature is favourable to the reaction with large activation energy, and low temperature is favourable to the one with lower activation energy-----

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

And the low temperature, that is the lower temperature will favour the one, that is the that reaction which is with relatively lower activation energy with this, you know means you can you can recall this expression and you can get a justification of this statement.

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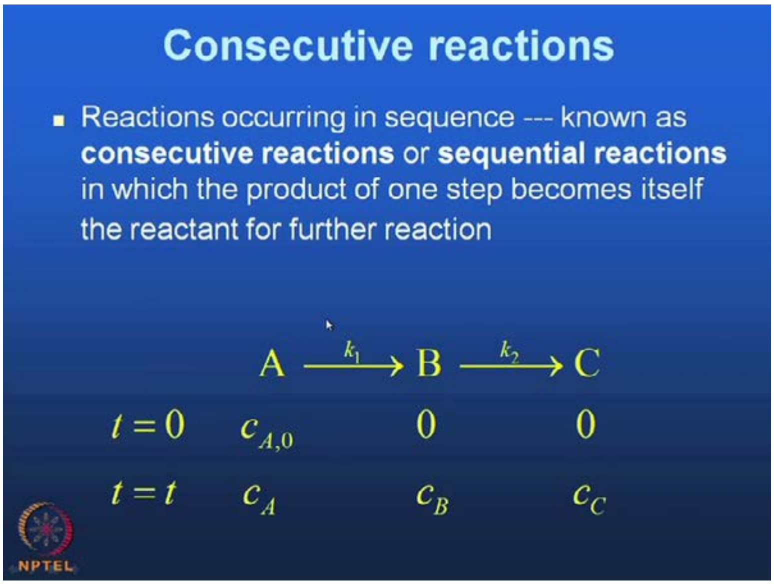

Consecutive reactions

- Reactions occurring in sequence --- known as **consecutive reactions** or **sequential reactions** in which the product of one step becomes itself the reactant for further reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

	A	B	C
$t = 0$	$c_{A,0}$	0	0
$t = t$	c_A	c_B	c_C

Next, we will move on to consecutive reaction, consecutive reaction means it is a sequential process, it is a sequential process.

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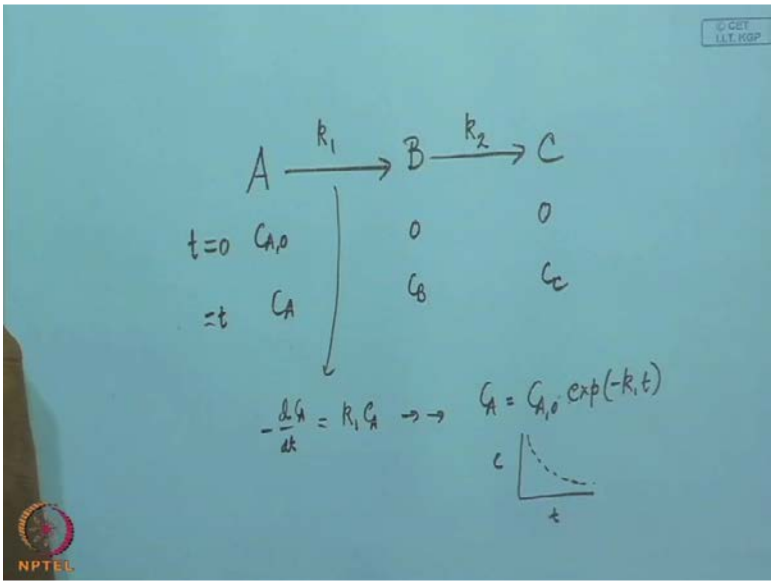

That is you have got A, is the starting material, that is giving you B, then B will be giving you C with k 1 and k 2 rate constants. So, at t equal to 0, t equal to 0, C A 0 it is this is 0, this is 0, at t equal to t, this is C A, that is the concentration of C A and this is C B and this is C C. So, this way you know reaction will will follow, so at the very start no B and no C is there, only A, the moment reaction has started, so slowly this will be produced and when the concentration of B is appreciable, then B will again start to get converted to C.

And this case we must remember one point, that may be there is a possibility of B to go back to A, but in that case those possibilities are neglected may be because that may happen, but with with A it is such a lower rate. That that is not you know you know we we cannot you know consider that, there is no point of considering such A, such a lower rate, so that is why this reaction is primarily A to B to C.

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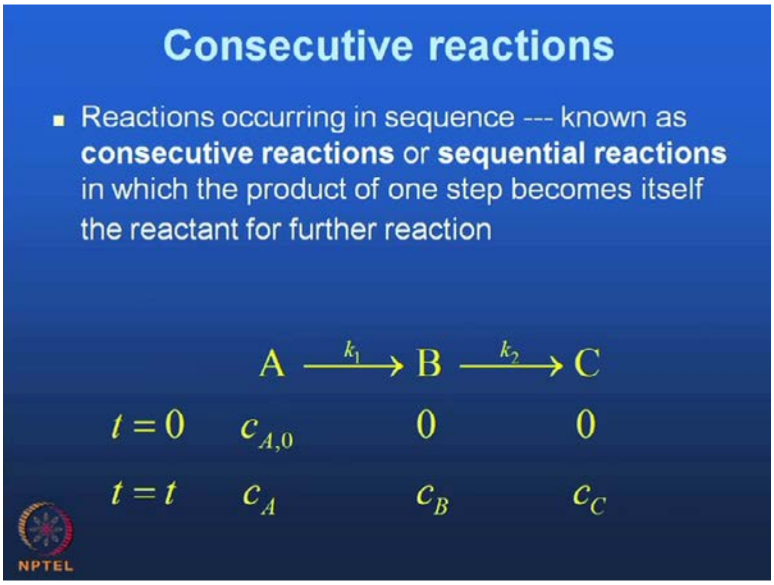

Consecutive reactions

- Reactions occurring in sequence --- known as **consecutive reactions** or **sequential reactions** in which the product of one step becomes itself the reactant for further reaction

$$\begin{array}{cccc} & A \xrightarrow{k_1} & B \xrightarrow{k_2} & C \\ t=0 & c_{A,0} & 0 & 0 \\ t=t & c_A & c_B & c_C \end{array}$$

So, reactions occurring in sequence known as consecutive or sequential reaction in which the product of one step becomes let us say the reactant for further reaction. So, this one is the product of A, this is becoming A reactant for this product, so d C A d t is equal to k 1 into C A. So, d C A d t with a negative sign is equal to k 1 into C A, if we integrate is we will be getting that C A after integration, there is a differential equation. When we integrate we will be getting C A is equal to C A 0 exponential minus k 1 t, so basically minus k 1 t means with increase of t, this quantity will be depleted, that means C A will be decreased in a first order fashion, exponentially decreased. So, this is concentration, it is time.

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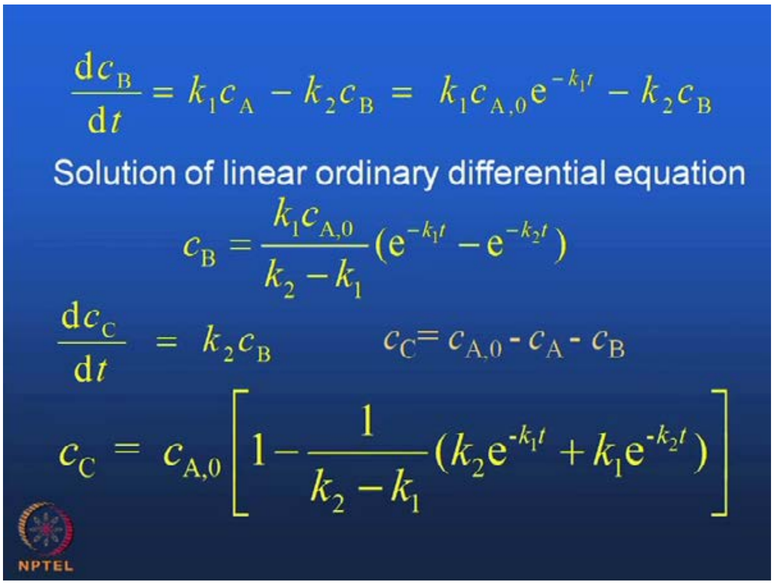

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B = k_1 c_{A,0} e^{-k_1 t} - k_2 c_B$$

Solution of linear ordinary differential equation

$$c_B = \frac{k_1 c_{A,0}}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$\frac{dc_C}{dt} = k_2 c_B \qquad c_C = c_{A,0} - c_A - c_B$$

$$c_C = c_{A,0}\left[1 - \frac{1}{k_2 - k_1}(k_2 e^{-k_1 t} + k_1 e^{-k_2 t})\right]$$

Now, d C B d t, now let us find what will be d C B d t that is the rate of formation of B.

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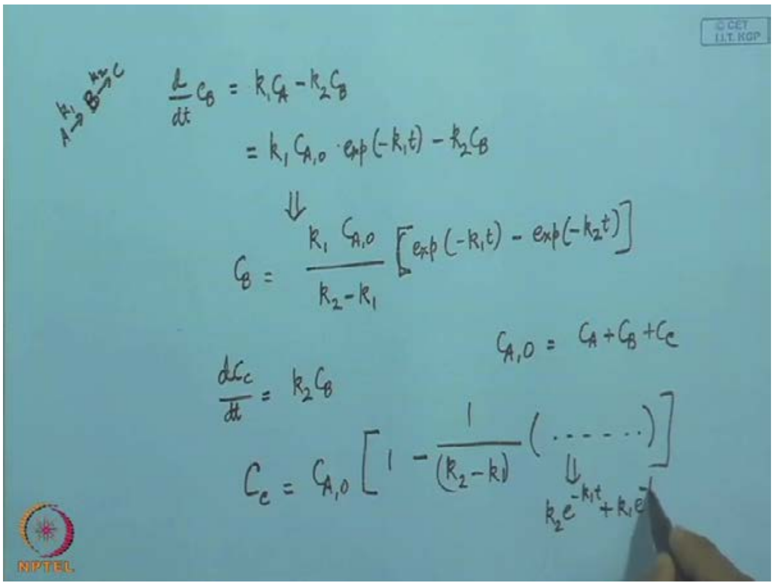

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

$$\frac{d}{dt} C_B = k_1 C_A - k_2 C_B$$

$$= k_1 C_{A,0} \cdot \exp(-k_1 t) - k_2 C_B$$

$$\Downarrow$$

$$C_B = \frac{k_1 C_{A,0}}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$$

$$C_{A,0} = C_A + C_B + C_C$$

$$\frac{dC_C}{dt} = k_2 C_B$$

$$C_C = C_{A,0}\left[1 - \frac{1}{(k_2 - k_1)}(\cdots\cdots)\right]$$

$$\Downarrow$$

$$k_2 e^{-k_1 t} + k_1 e$$

So, d d t of C B, because we are looking at the formation rate of B, that is why it is in plus sign, is equal to k 1 C A. Recall the initial prescription that A to B to C k 1, k 2, so B is produced with k 1 rate that is why it is in plus sign, this is depleted with k 2 rate that is why it is in minus sign. So, minus k 2 C B, so that means recall the earlier lesson that C A is equal to C A 0 into exponential minus k 1 t, so that you just plug in over here, so C A 0 into exponential minus k 1 t minus k 2 C b. So, solution will be like you know if you give this solution it is A it is an ordinary differential equation, your solution will be C B is equal to k 1, you can try this by yourself, C A 0 divided by k 2 minus k 1 exponential to the power minus k 1 t minus exponential to the power minus k 2 t.

And also d C d t is equal to k 2 C, because the C is produced only from B, only from B that is why this is got only one term, only single term. And also C A 0 is equal to C A plus C B plus C C, so instantaneous is A B C at any moment, the remaining A produced B and produce C or may be remaining A, remaining B and produce C. So, then the concentration of C, C C will be equal to C A 0, this will come out like this, 1 minus 1 by k 2 minus k 1 into this exponential quantity. So, exponential quantity, there will be two exponential quantities, k 2 exponential minus k 1 t plus k 1 exponential minus k 2 t, basically this one will be k 2 exponential minus k 1 t plus k 1 exponential minus k 2 t.

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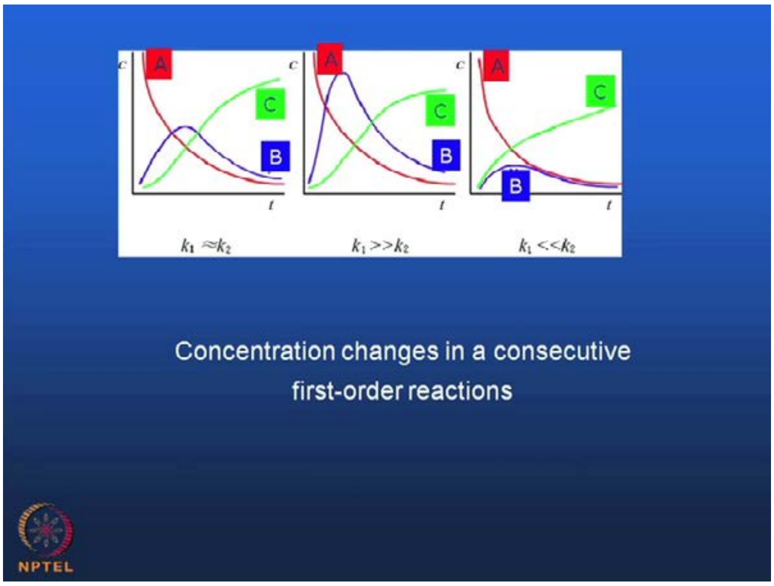


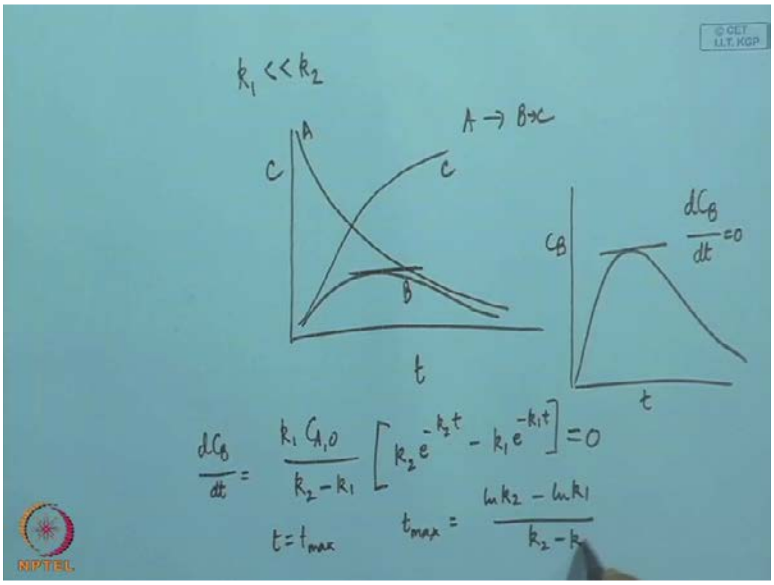
Concentration changes in a consecutive first-order reactions

So, now, if we focus on to, if you focus on to concentration of various species present in solution, for such a consecutive, consecutive first order case, then you you can have three situations. We can have three situations, that one is k 1 is close to k 2, that is A to B to C k 1, k 2, so these two rate I mean rate constants are very close, then the plot will be like the typical plot. This is concentration C, this is time, so this your A, so it is depleted, because you know anyway it is depleted to B in a first order kinetics, therefore it is always decaying like this.

And your B will be, it is growing, it will grow, but the problem is after it has grown to certain extent like this to such a concentration then this reaction becomes appreciable. When this concentration is low, then maybe it is still doing this reaction, still be doing this reaction, but the thing is that if it is not appreciable, this concentration is not appreciable, the effect of this step will not be not be you know you would not you would not be able to feel the effect of this step. That is why up to certain point it will keep on rising and then eventually it will decay because of the second you know step of k 2. And what about you know the C, C will follow like this, so this is your C, this is your A and this is your B. So, when k 1 and k 2, these two are you know these two are almost close to each other and when these two are close that is why may be the maxima is in the in the midpoint, midpoint of this graph, may be is this maxima is at the midpoint of this graph.

So, when this is you know showing a maxima, because it is growing, this step is a growth factor for this B, that is with, so this particular step is importantly rising trend, rising trend on B and this one is a decaying trend. So, when rising decay these two match, then you know or when they compete with each other with equal strength then they are they are that is neither rise nor decay, that is why it is passing through through the maxima with a slow pace, that is with with a slow pace d C d t d C B d t is equal to 0. You see here this is b, so here d C B d t is equal to 0 that is with time the concentration of B is not changing, so this is one situation where k 1 is very close to k 2.

Now, let us move on to another case, when k 1 is greater than k 2 that is the effect of this step, so A to B to C, k 1, k 2, so that means this is very strong, this is relatively weak.



That is why k 1 is very very greater than k 2, so what will happen, if you plot, if you plot so A will be as usual with decaying trend. So, A is concentration versus time and you know this maximum will be near your this axis, eventually it will it will decay and your this one will be something like like this. So, this is your B and this is c, so this is B and this is c, so why it is like this, because you know since k 1 is very higher therefore at a very high rate it will reach the top. In in previous case the the maxima was at some some intermediate time here, but here this maxima is here, much earlier than this maximum, when k this is for your k 1 is close to k 2 and here k 1 is very very greater than k 2.

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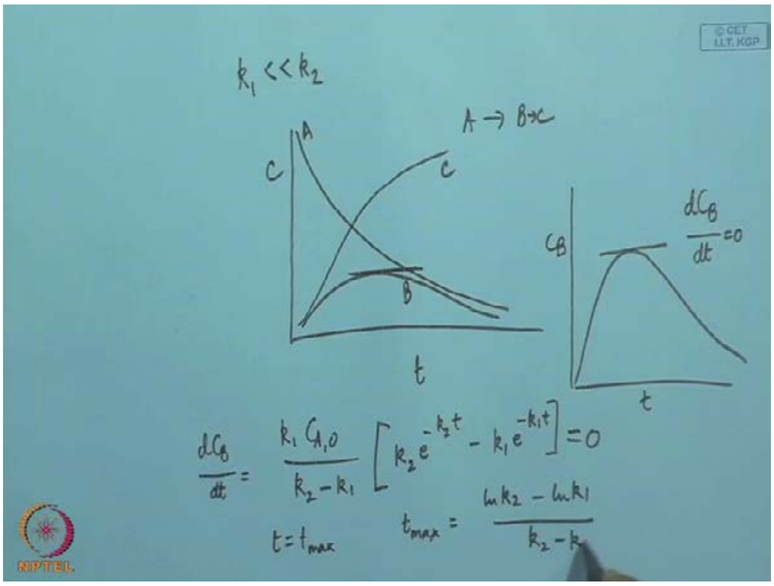

$k_1 << k_2$

$A \to B \to C$

$$\frac{dC_B}{dt} = \frac{k_1 C_{A,0}}{k_2 - k_1}\left[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}\right] = 0$$

$t = t_{max}$

$$t_{max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}$$

So, that is the effect of k 1 is so high that it gives you this maximum here and then it is depleted after certain time, it is slowly depleted and C is as usual it is going up, it is going up, that is kind of an exponential you know growth. So, again this is also a case where you know this is this is a rising function and that is the decaying function that is why it is passing through a maximum.

The third case is k 1 is very very less than k 2, so very very less than k 2 or may be less than k 2, so this is concentration versus time. So, A is as usual like this, exponentially decaying and what will happen to B, because it will not show A you know prominent maximum because the moment it is created, this B is created it is quickly depleted to C, so A to B to C. So, concentration of B is not beat up to a sufficient extent as a result of which you know this one is less, that is your maximum concentration or or I mean you know t at which this is this C B is maximum you know it takes long time, because it is slowly growing and is fast decaying. And you know as usual your C is like this, so this is A, this is B and this is C, so these are the three possible situations that one can think of.

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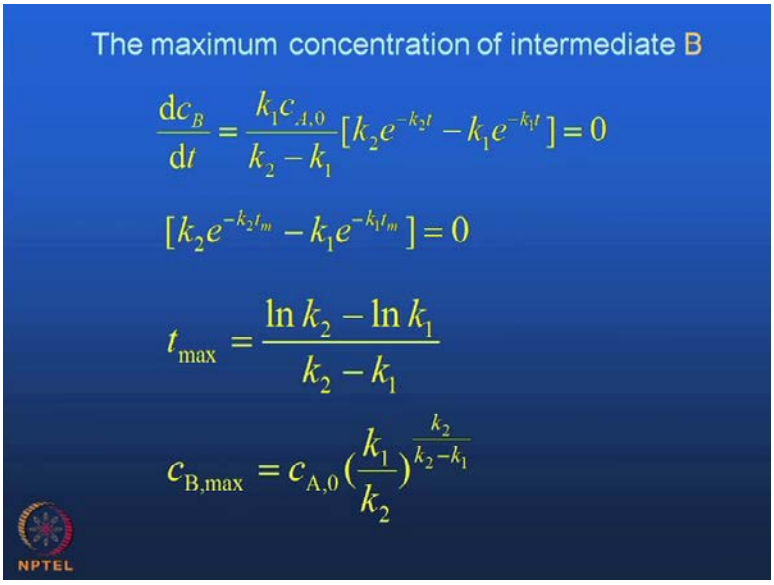

The maximum concentration of intermediate B

$$\frac{dc_B}{dt} = \frac{k_1 c_{A,0}}{k_2 - k_1}[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}] = 0$$

$$[k_2 e^{-k_2 t_m} - k_1 e^{-k_1 t_m}] = 0$$

$$t_{\max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}$$

$$c_{B,\max} = c_{A,0}(\frac{k_1}{k_2})^{\frac{k_2}{k_2 - k_1}}$$

So, then how to find out this maximum concentration of the intermediate or may be the time when this is this reaches the maximum. So, it is easy, as I told you that if we have a plot for you know this B it is like this, may be it is a it is a typical plot. So, concentration of B versus t, so d C B d t is equal to 0, d C B d t will be equal to 0, therefore what we have to do is we have to, this is called the extremum situation, so we need to find find the extremum condition. So, d C B d t is equal to k 1 C A 0, recall earlier slides, so k 2 minus k 1, then k 2 exponential minus k 2 exponential, ok. Let’s go back to earlier slide, d C B d t, this is your d C B d t, so you have to have to use this expression.

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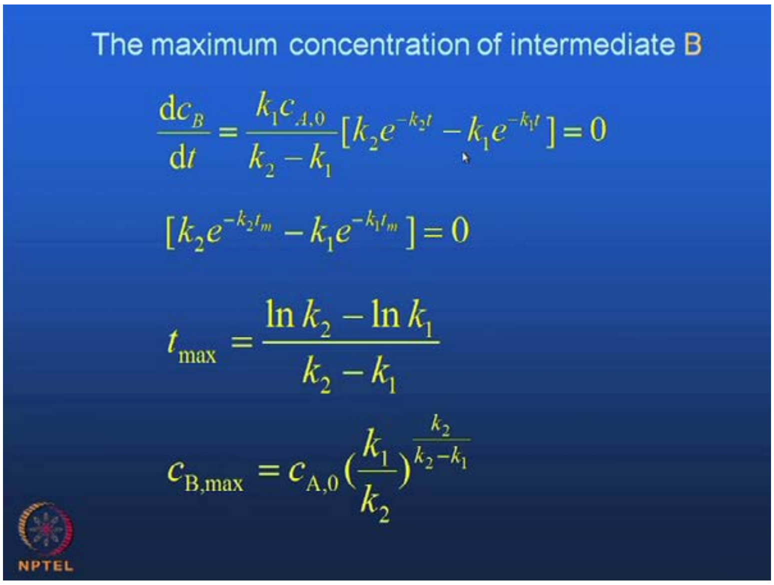

The maximum concentration of intermediate B

$$\frac{\mathrm{d}c_B}{\mathrm{d}t} = \frac{k_1 c_{A,0}}{k_2 - k_1}[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}] = 0$$

$$[k_2 e^{-k_2 t_m} - k_1 e^{-k_1 t_m}] = 0$$

$$t_{\max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}$$

$$c_{\mathrm{B,max}} = c_{\mathrm{A},0}\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}}$$

So, so k 2 exponential exponential minus k 2 t minus k 1 exponential minus k 1 t, you just recall equal to 0. So, equal to 0 means this is 0, this is 0 means t max, that is for t equal to t max, so t equal to t max, t max, so t max will be equal to will be equal to l n k 2 minus l n k 1 by k 2 minus k 1. So, C B max will be will be equal to that is the concentration of B at t max.

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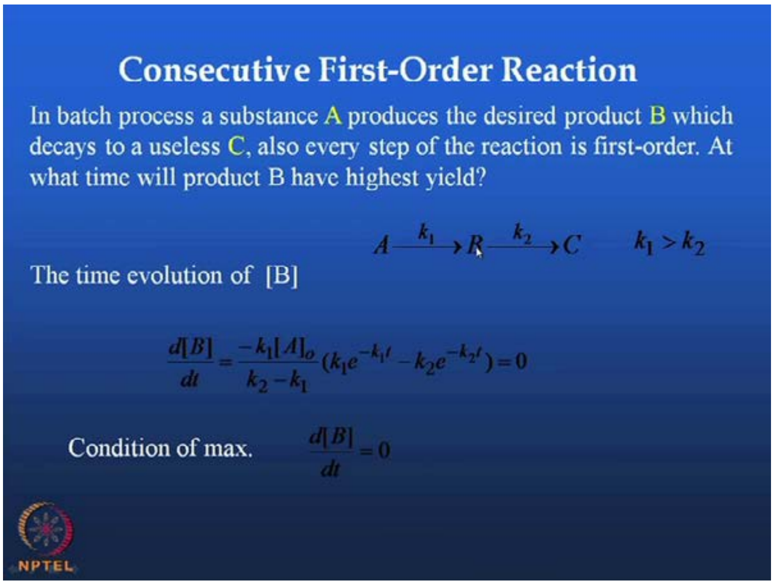

Consecutive First-Order Reaction

In batch process a substance A produces the desired product B which decays to a useless C, also every step of the reaction is first-order. At what time will product B have highest yield?

$$A \xrightarrow{k_1} R \xrightarrow{k_2} C \qquad k_1 > k_2$$

The time evolution of [B]

$$\frac{d[B]}{dt} = \frac{-k_1[A]_o}{k_2 - k_1}(k_1 e^{-k_1 t} - k_2 e^{-k_2 t}) = 0$$

Condition of max. $\frac{d[B]}{dt} = 0$

So, C B max, C B max, so maximum concentration of B will be equal to C A 0 k 1 by k 2 into k 2 divided by k 2 minus k 1. So, what is the utility of such description, this is that a tremendous utility, that if you think of industrial processes, if you think of industrial processes like A, which is producing the desired product B and then your desired product may undergo some side reaction or may be some other reaction which is an undesired, one which is useless, may be which is useless to you. And also think that may be this these two steps are first order, first simplicity and also k 1 is greater than k 2. k 1 is greater than k 2 means the the case which we discussed let us go back to the slide where these plots are giving k 1, k 2, so we will we will refer to this plot may be.

So, our question is at what time will product B have the highest yield, that means we need to calculate the time and then maybe we have to isolate isolate your reaction mixture may be during that that time when. Means your calculated time say may be at say may be after 1 hour of your start of reaction if you calculate that your concentration of B will be maximum. Then just after 1 hour, you just take out your reaction mixture and then you try to isolate your B as early as possible, so that it you you will be getting maximum yield of B. Of course with the condition of k 1 is greater than k 2, may be if k 1 is you know less than k 2 or something else then the situation may be different. So, what I will do, we will we will first look into time evolution, time evolution of B, that is time variation of B. So, so d B d t is equal to, as I as I gave you the expression that k minus k 1 A 0, A 0 means your your starting concentration k 2 minus k 1. So, you have to like do do this exercise of course with a assumption that this step is first order, this step is first order. If it is the first order or something else then you know you cannot help with this expression, with these equations, you have to think of something else.

So, that means you need to extremize it, because you would like to find out this, the condition, when this happens, like this happens, so the idea is that you have to look for this one. So, this is concentration versus time, so you just extremize it, you extremize it, so upon extremization you put that equal to 0 and also also that that your A 0 is not 0 and k 1 is also 0, k 1 is also not zero. So, with those conditions, as I as I told you that this as already I stated that t m maximum is equal to l n k 2 by k 1 k 2 minus k 1, so you can find out the maximum concentration of B, that is B maxima, which is like this B max is equal to this as I just wrote. So, this way you know you should be able to find out, you should be able to to find out you know the maximum concentration of B, ok.

So, for k 1 greater than k 2 as k 2 increases, so if k 2 increases then what will happen, so this k 2 increases, if k 2 increases what will happen, if this increases, this increases and this also increases. So, this increases means this denominator is becoming less, this is increasing and this is increasing although this is increasing, means this factor is increasing, but as a result of which what will happen that since the power factor is more to the power factor so both time, so as it increases both the time, when B is maximum and the yield of B these two will go up.

So, that is why there is a there is a there is a you know relation, because this relation gives you how you can modulate this B max. You can modulate this B maximum by changing, you know somehow you can, if you can change this k 2 may be increasing temperature or something else, so that is why if your k 1 greater that k 2 as k 2 increases, both the time when B is maximum, so this is, B is maximum and also in that B, this these two you know go up.

So, you know that is why consecutive reaction, it is a it is a very I mean although I have discussed this first order case, but anyway this is just to give you the idea that if side reactions are happening like consecutive reaction, of course it is of this reaction, you know the reaction with which we have started our talk with consecutive first order reaction. That you know say this is the desired reaction and say this is your side reaction, if you think that this is your side reaction and then it is a real problem, you know in industrial batch production, so this your headache. So, in that what we have to do you need to just tactfully calculate, you have to calculate this, you know time when B is maximum, so if B is maximum means the time when B is maximizes, so at that time you try to isolate, you try to isolate you you know reaction mixture.

So, you try to isolate your reaction mixture and then try to workup, workup means try recover your B product, so this is very important. So, you see this consecutive reaction has got a very you know you know this has got an immense importance in industrial preparations. So, what you have learnt you know in this particular discussion on complex reaction, so first we have to we have to recall this thing, what is an elementary reaction, it is a very important point elementary reaction. Elementary reaction means a complex reaction, a complex reaction can be regarded as a combination of more than one elementary steps. So, elementary steps means at least it will have two elementary steps, an elementary steps are steps where you can just see as if two components or may be one component is directly giving you the product, directly giving you the product.

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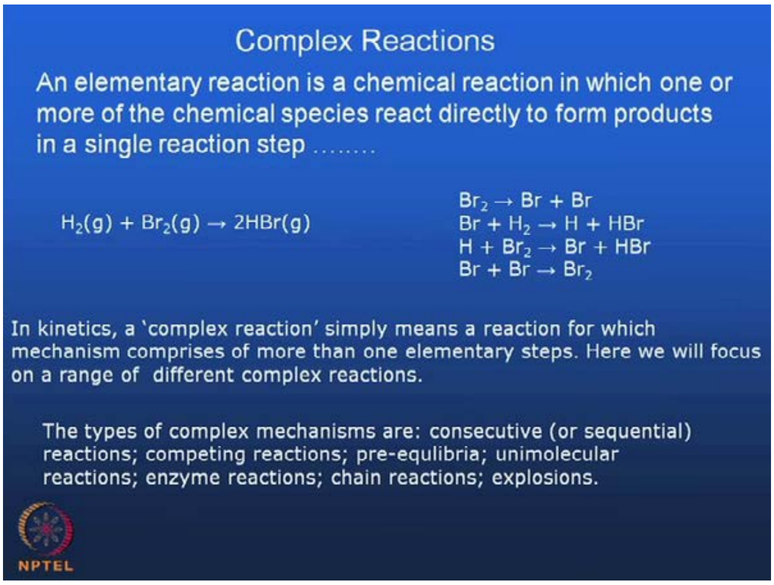

Complex Reactions

An elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step ……..

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$Br_2 \rightarrow Br + Br$
$Br + H_2 \rightarrow H + HBr$
$H + Br_2 \rightarrow Br + HBr$
$Br + Br \rightarrow Br_2$

In kinetics, a 'complex reaction' simply means a reaction for which mechanism comprises of more than one elementary steps. Here we will focus on a range of different complex reactions.

The types of complex mechanisms are: consecutive (or sequential) reactions; competing reactions; pre-equlibria; unimolecular reactions; enzyme reactions; chain reactions; explosions.

So, since as you see whether the example you know example with which I have started to the discussion, that this particular reaction has got four elementary steps and you see two species here, two species, two species, one species. So, these three are you know bimolecular step, this is an unimolecular step you can call and we have classified this complex reactions like consecutive reaction, competing reaction, per-equilibria, then unimolecular reaction, another is you know (( )) reaction, that is enzyme reaction, enzyme catalyzed reaction, chain reaction, we will come to that you know in in later lecture and then explosion.

Then we have discussed this opposing reaction that is one reaction which is opposed by another reaction producing your reactant back, so and also from this opposi you know starting this opposing reaction kinetics you can find out the k for both forward and backward steps, of course we have to know the equilibrium constant and that we can find out from other measurements, that is equilibrium measurements. We have given an example, of course be careful about these units, then to use these units this is just to make sure that which unit we are using for calibrating it. So, forget about this unit, try to find out units for these you know steps by your own, it is not a difficult task.

Next is parallel reaction, parallel reaction you know what we have discussed over here is parallel reaction of which both you know parallel steps are first order type. So, it is a simply first order parallel or competing reaction and basically you know your reactant is depleted in first order kinetics and the products are formed, that is products are parallel reactions you know formed you know like a you know exponential growth and you can also find that k 1 and k 2, of course knowing k 1 by k 2 for this parallel reaction. And of course, temperature has got an immense importance on which step is the favoured or not that you can find out using this arrhenius equation.

Consecutive reaction, it is A to B to C, where B is an intermediate may be or maybe it is your desired product also. So, with k 1 and k 2, under various conditions, when k 1 is greater than k 2 or k 1 is lesser than k 2 or k 1 is equal to k 2, you can find out the situation which is you know the picture in the graph like case 1, case 2 and case 3. So, in every case you are finding that this B is passing through a maximum and A is depleting and C is growing, because B is the intermediate, which is formed out of A and it is depleted to give you C.

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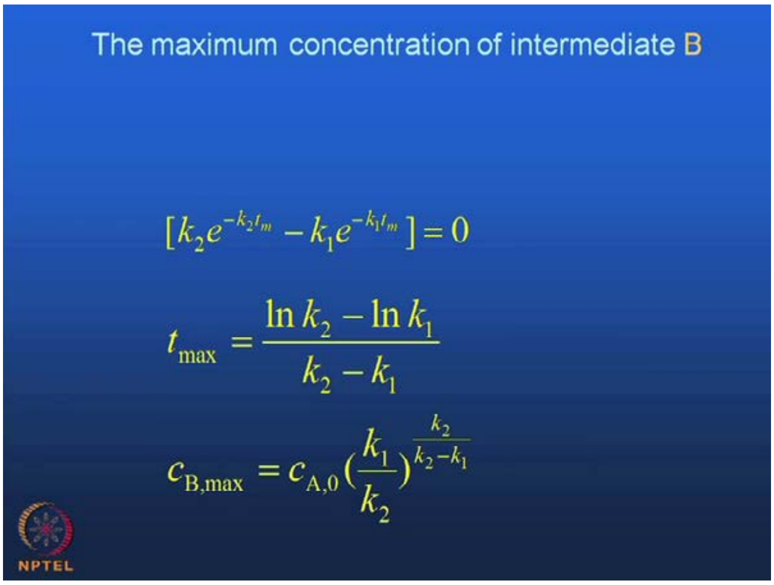

The maximum concentration of intermediate B

$$[k_2 e^{-k_2 t_m} - k_1 e^{-k_1 t_m}] = 0$$

$$t_{\max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}$$

$$c_{B,\max} = c_{A,0} \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}}$$

And this is got importance in your industrial application that you can find out the time at which this intermediate will be maximum or not, at what time is maximum that you can find out. And from that you can get our desired product at the maximum yield, means after certain after that time suppose if you if you calculate the time t m after t m you can impressively find out the you know the desired product and means when this desired desired product will be a maximum concentration.

So, in our next lecture, we will talk more on complex reactions and we will take up like other reactions I just you know pointed out when we started the this particular lecture. So, till then have nice time and we will meet in the next class with more examples on complex reactions, thank you.