

## Chemical Kinetics and Transition State Theory

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Lecture no 02

Its elementary – rate law equations

Hello and welcome to the second module of Chemical Kinetics in Transition State Theory. In this module we are going to finish up a preview of the pre-requisites. So, today we will cover how to think of elementary reactions, reaction mechanisms and finally end up with how to write rate law equations.

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### Resources

1. Chemical kinetics by K. Laidler, Chapter 1
2. NCERT book, Class XII, Part 1, Chapter 4: <https://ncert.nic.in/textbook.php>
3. [https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Kinetics/Reaction\\_Rates/Reaction\\_Rate](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Rates/Reaction_Rate)

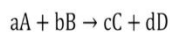


So, again the resources are the same as that of module 1, we are following the chapter 1 of the Laidler's book, you can find essentially the same information in the NCERT book class 12 chapter 4 and I have also provided you here a link where you can find the information online as well.

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## Rate of a reaction

For the reaction



$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

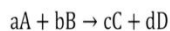


So, let us begin a brief summary of what we covered in the module 1, if you have a reaction of the type that is written here  $aA + bB \rightarrow cC + dD$ , where rate of this reaction we proofed in the last module under the condition of constant volume is given below here, it is given by  $\frac{-1dA}{adt} = \frac{-1dB}{bdt} = \frac{+1dC}{cdt}$  and so on. So, it is important to note, we use a negative sign for reactants and a positive sign for products.

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## Order of reaction and rate constant

For the reaction



Empirical observation

$$\text{rate} = k [A]^{\alpha} [B]^{\beta}$$

Rate constant

$k \equiv$  rate constant.  
is independent of  $[A]$  &  $[B]$   
 $k [T]$



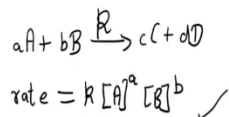
So, now we move forward and look at how to calculate the rate constant and the reaction order. So, we start with the same reaction as before, we look at  $aA + bB \rightarrow cC + dD$ . For this reaction, more often than not one can experimentally observe that the rate that was defined in the previous slide can be written as  $k[A]^\alpha [B]^\beta$ , where  $k$ ,  $\alpha$  and  $\beta$  are numbers. Ok

Our focus in this course will be on this parameter called  $k$ . So,  $k$  is what is called the rate constant, I emphasize again that this rate constant holds only when this empirical observation  $\text{rate} = k[A]^\alpha [B]^\beta$  holds. Another important thing to note which is often missed by many students is that this rate constant is independent of concentration of A and concentration of B, that is by definition,  $k$  is simply a number but it does depend on temperature,  $k$  does depend on temperature. So, we will be looking in this course specifically how to calculate this  $k$  as a function of temperature.

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## Elementary reaction

An elementary reaction is a chemical reaction where reactants combine directly to give products without any reaction intermediate.



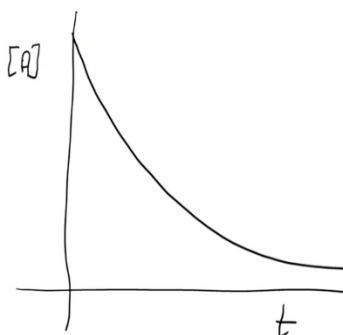
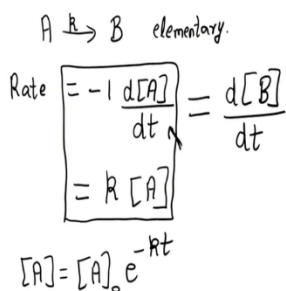
So, there are reactions themselves can be divided into 2 parts. A reaction that is elementary and a reaction that is complex. An elementary reaction is a 1 where the reactants combine together to give the products in 1 step without any reaction intermediate. So, essentially what is happening is that your reactants are combining together in directly as a form of a collision you can say and just giving the product there is nothing in between.

So, for an elementary reaction 1 very important observation is that the rate is always given as  $k[A]^a [B]^b$  for a chemical reaction, for an elementary reaction of the form. So, if a reaction is

elementary this equation must hold always, no exceptions. So, we often write the rate constant here above the arrow to signify that this equation will hold.

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Example: first order reaction



So, well let us just take 1 example of a 1<sup>st</sup> order reaction. Again, you must have seen this before, so we are going to go through this slightly quickly just to revise what you already know. Reaction can be of many orders, it can be zero order, 1<sup>st</sup> order or 2<sup>nd</sup> order. 1<sup>st</sup> order specifically is of the form A going to some products B. The important thing is reactant is only 1 molecule.

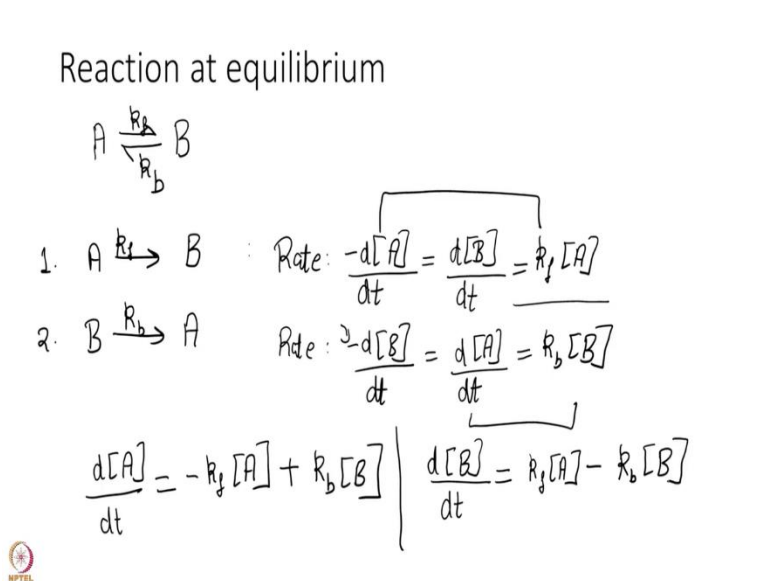
So, let's say I have this reaction and this is elementary, so for this reaction 2 conditions must hold true as we have looked at. First is rate must equal  $-1 \cdot dA/dt$ . So, note that the stoichiometry coefficient here is 1, so I have simply -1 here and a negative sign because A is a reactant and this will also be  $= dB/dt$  correct.

If it is elementary another condition holds, the 2<sup>nd</sup> condition is that the rate must also equals  $k$  concentration of A. So, I will equate (6:48) these 2 equations and I will just write down the solution, we are recapping here, so I am moving slightly faster. The solution for this differential equation is given by this.

So, I will leave this as a homework to verify if this solution is true or not. So, to do that you must fit in the solution into this differential equation, the left hand side and the right hand side and verify. Well, now we have gained some information after all these definitions, if I make a plot of

a 1<sup>st</sup> order reaction, of any 1<sup>st</sup> order reaction, it will always have this characteristic decay. So, an example of this is for example a radioactive decay, if you take uranium it is decaying and if I look at the population of uranium, it will decay in this exponential form.

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So, moving forward how to write these kind of rate law equations, we will take a few examples in today's module. So, the first thing that I want to look at is a reaction at equilibrium. A reaction at equilibrium, we will look at an example of a reaction at equilibrium. A reaction at equilibrium essentially has the form.

So, not only can you go from  $A \rightarrow B$  with some rate constant  $k_f$ , you can also go from  $B \rightarrow A$  with some rate constant  $k_b$ . And I ask you that, I tell you that this is elementary both sides and I want you to be able to write the rate law equation for this. How do I handle that? The trick of this is to divide this equation in 2 steps.

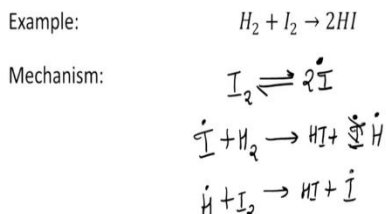
1, we write the forward part only and 2 we write the backward part only with the corresponding rate constants. So, 1 is  $k_f$ , the other is  $k_b$ . So, now we treat both of them independently to start out with and then we calculate the rate of this is  $-dA/dt = dB/dt = k_f * A$ . I emphasize this portion only has the reactant concentrations in it. For this first step, A is the reactant, for the second step I will treat B as the reactant, whatever is on the left side of the arrow.

So, for this one I will write the corresponding rate as  $-dB/dt = dA/dt = k_b [B]$  ok. Now, if I want to calculate  $dA/dt$ , how do I calculate that? The idea is we need to add the corresponding elements in the 2 equations, so we look at the 1<sup>st</sup> equation, the 1<sup>st</sup> equation tells me  $dA/dt$  is  $-k_f A$ , so we look at this term and note that I had a negative sign before  $dA/dt$  so I put that negative sign in the right hand side and I get  $-k_f A$ .

And I look at the 2<sup>nd</sup> equation that also has a  $dA/dt$ , so I take that and I add  $k_b B$ , so that is my first equation for  $dA/dt$ . I can write a corresponding equation for  $dB/dt$ ,  $dB/dt$  again appears twice in both equations, and from the 1<sup>st</sup> equation the contribution is positive  $k_f A$  and if you see that in the 2<sup>nd</sup> equation, I have a negative sign here so I have a  $-k_b B$ . So, this is how you write rate law equation for complex equations.

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### Reaction mechanism



So, once you have elementary reactions what can you do with them? You can essentially construct mechanism of any reaction in terms of elementary reactions, so in some sense elementary reactions act as atoms of chemical reactions, you give me a chemical reaction and I will be able to figure out some combination of elementary reactions that will give me that full reaction.

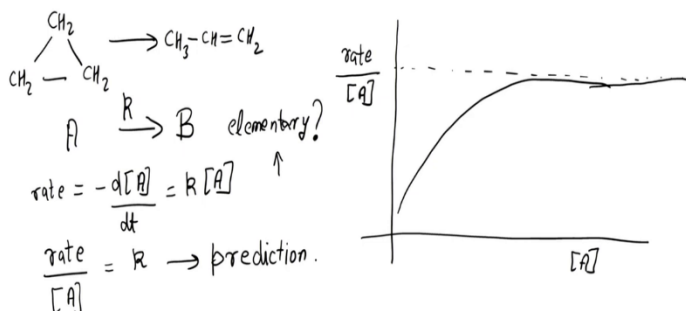
So, a very well cited example is  $H_2 + I_2 \rightarrow 2HI$ . This was long thought to be elementary but evidence showed that for this reaction  $H_2 + I_2 \rightarrow 2HI$  the mechanism actually turns out to be that

$I_2$  in equilibrium first dissociates into  $2\dot{I}$ ,  $\dot{I}$  reacts with  $H_2$  to give  $HI + \dot{I}$ , my apologies this should be  $\dot{H}$ .

$\dot{H}$  reacts with  $I_2$  to give  $HI + \dot{I}$ , so this is an example of what is called a chain reaction, if we generate these radicals and they will keep on propagating till the radical population goes away. So, you do not have to memorize this reaction or the reaction mechanism, it's simply an example, an illustration of how reaction mechanisms can be broken down into elementary reactions. I want to end today's module with a discussion of a very interesting case, which was very deeply studied and hotly debated in 1920s, which is the isomerization of cyclopropane.

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The curious case of isomerization  
of cyclopropane



Cyclopropane is a 3 membered ring, and as it turns out under appropriate conditions this can turn into propene. One fact that let me tell you this is unimolecular, there is no other molecule that this cyclopropane is interacting with to give propene. It is isomerizing on its own. So, that is experimental fact number 1 ok.

Just for ease, let me write this as A and let me write this as B. Well, in 1910s and 1920s, people were studying reactions of this form and this particular case of cyclopropane got a lot of attention, people were trying to understand its mechanisms, some people were trying to find the elementary reactions behind it.

And well, many people argued you have only 1 molecule, what else can possibly be the mechanism? And so the most natural thing to write is that this reaction itself is elementary, let us assume it is elementary, I do not know, I am not claiming it is elementary, but let's start by assuming that seems like a natural approximation after all.

If I assume it is true, well we have already derived for a 1<sup>st</sup> order equation,  $\text{rate} = -dA/dt = kA$ . Well, let me just rearrange it in a form that was experimentally observed, so this is my prediction, if I hold the hypothesis that  $A \rightarrow B$  is elementary, then I predicted rate over concentration of A must be a constant, must be a number. I again highlight that k is independent of concentration of A.

So, what people did is, they were smart experimentalists, they plotted rate divided by concentration of A as a function of concentration of A. So, take a little pause and draw this graph on your own first on what you expect if this hypothesis is true. So, please pause the video and fill in this graph on your own.

Hope you have an answer with you, a graph with you. What I expect is basically a straight line, well that is simple right, because I have already shown that  $\text{rate}/A$  must be  $= k$  and k is a number at a given temperature. So, therefore I expected a straight line, but look and behold what the experimentalists observed, the curve goes (17:39) like this.

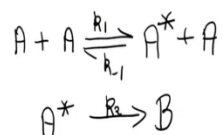
So, at large concentration everything is good, but the hypothesis is clearly breaking down at low concentrations. And that led to a hot debate on what can be the mechanism. So, clearly by hypothesis is wrong, my hypothesis does not tests with the experimental results. So, what I will just briefly describe is what was put forward by Lindemann-Christiansen in 1920s as a way to resolve this problem.



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The curious case of isomerization  
of cyclopropane :

Lindemann-Christiansen hypothesis

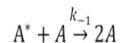
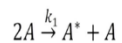


And I am showing this example, again do not memorize these things, but this is an example to show how the knowledge of elementary reactions and their rate laws can help us understand what is going on an atomic level. So, this is the hypothesis that Lindeman and Christiansen put forward. They said A and A, A again is my cyclopropane, A actually, 2 molecules of A first collide with each other, they react with each other in a reversible fashion to give me an excited  $A^* + A$ , this is the hypothesis, they are just pulling around.

And they had put a 2 forward and backward rate constant, I am just following the language they had used, so I am using  $k_1$  and  $k_{-1}$ . And  $A^*$  which an activated state gives rise to B. So, this is a more detailed mechanism, now it is not a simple. Now, we have a more complex reaction and what I want to discuss in this module is how do we write rate laws for this and can we perhaps resolve the contradiction with experiment using this hypothesis. So, let's get to how to write rate law equations.

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Writing rate laws:  $B$



$$\frac{d[B]}{dt} = k_2 [A^*]$$

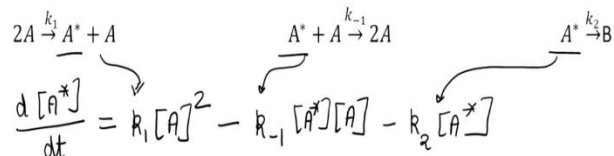


So, we will, we have 3 components here A, B and  $A^*$ , we will start with writing the rate law for B, it will become clear why, it is the easiest to write,  $A^*$  is next level difficulty and A is complex. So, we will go from easy to hard. So, let's start with B. So, here what I have already shown you are the 3 reactions, the forward reaction of the first step of the last slide, the backward reaction and the third reaction  $A^* \rightarrow B$ .

So, to write rate law we will follow the same scheme as I told for equilibrium reactions ok. So, if I have to find  $dB/dt$ . Well, the first thing to note in which of the equations above is B appearing. I note that B appears only and only here, B here is a product, so this will be equal to  $k_2 A^*$ , yeah its positive because its product side and I use  $k_2 A^*$ , A star is the reactant. So, B is easy we move on to  $A^*$ .

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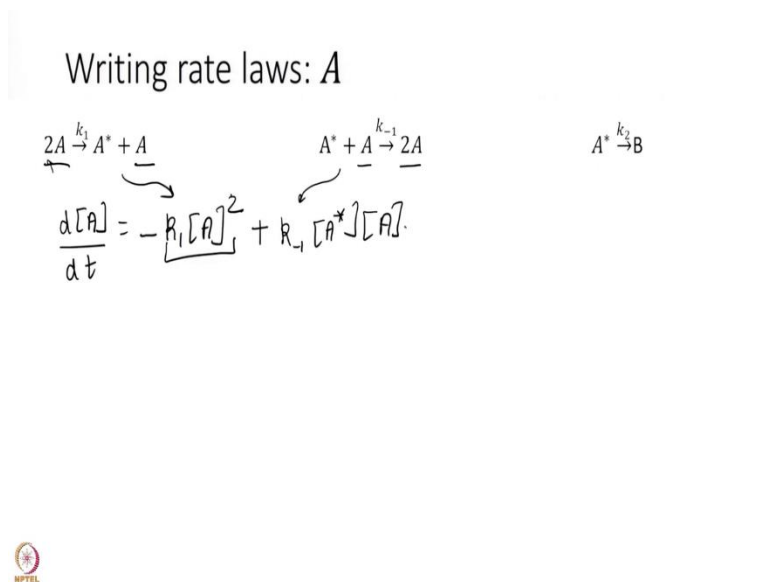
Writing rate laws:  $A^*$



Again, I ask you where all do you see  $A^*$  in all of these equations. I find  $A^*$  is here, I find  $A^*$  is here, and I find  $A^*$  is here. So, all I have to do is to take the components of each of them and add them together. So, I start, I write  $dA^*/dt$ ,  $dA^*/dt$  for the first one will be  $k_1 A^2$ . So, this one is positive because  $A^*$  is a product here and I get  $A^2$  because of the stoichiometric coefficient 2 behind A.

Second one is this,  $A^*$  is a reactant here, so I get a  $-k_{-1} A^* A$ . Finally, I use this one again  $A^*$  is a reactant, so I get this. So, we have discussed it for  $A^*$ , let us discuss for A and let's see where all A is coming.

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So, A comes many many times and so the challenge is how do you write a rate equation for this. Pause the video, write the rate equation on your own, this one is slightly more challenging, it's a harder problem but you have full information on how to solve it. Please pause the video now and I will show you the solution after you have solved it on your own.

So, hopefully you have an equation with you, if you are not able to solve it, do not worry, let us solve it together now. For this lets use the same steps as we have done for B and A\*, let us focus on this equation first and here is the question, is A a reactant or a product? It is both, what do I do?

Well, let us not panic, what you do is go back to the fundamentals, how is rate defined, rate is defined based on extent of the reaction, it is a differential of extent of reaction with time. How is extent defined? It is defined on the consumption or production of a given element or molecule. So, what is the extent here if 2 moles of A is consumed, 1 mole of A will be produced.

Therefore, the extent is 1 mole of A is consumed overall. So, what we have is a  $-k_1A^2$ . So, the - sign comes because A is consumed by 1 mole as the extent and this component is simply rate constant into reactants nothing more, no more thinking on that. And I have a coefficient 2 here, so I write a 2 here, irrelevant of whether A was in the product or not.

So, I do the same thing on this side, now here correspondingly I will get a + because for every mole of A that is consumed 2 moles of A is being produced so in effect 1 mole of A is being

produced and I blindly write the rate constant into product of reactants ok. We will have more problems of this in the assignment, where you will get more practice on how to solve these problems.

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## Steady state hypothesis

The population of intermediates do not change with time

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$



So how do we make progress beyond this? What we do is to make what is called the steady state hypothesis. What this hypothesis states, and again moving a little fast, this hypothesis states that the intermediates, concentration do not change with time. And the intermediates are the one which do not appear in the overall reaction. So, in this case that is  $A^*$ , A is the reactant, B is the product and the intermediate in between is  $A^*$ .

So, I have written back the equation corresponding to  $dA^*/dt$  that I derived 2 slides before and what steady state hypothesis says is this is equal to 0. So, I will just use this equation and simplify a little bit, so I just take find out what is the concentration of the intermediate here and eliminate it out. So, this one you can verify is equal to, so this is simple algebra, you can look at it and convince yourself, this is true. So, we get concentration of  $A^*$ , but what we are after remember is the rate.

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The curious case of isomerization  
of cyclopropane

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$



$$\begin{aligned} \text{rate} &= -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_2[A^*] \\ &= \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \end{aligned}$$



Now, our overall reaction is  $A \rightarrow B$ . So, the rate is  $-dA/dt = dB/dt$ , but  $dB/dt$  we showed  $= k_2 * A^*$ . Remember we solved for both all 3 A, B and  $A^*$ . And  $dB/dt$  you can look back, comes out to be  $k_2 * A^*$ . Well, I know now  $A^*$ , so I will feed that here and I get this. So, I have now an equation for the rate.

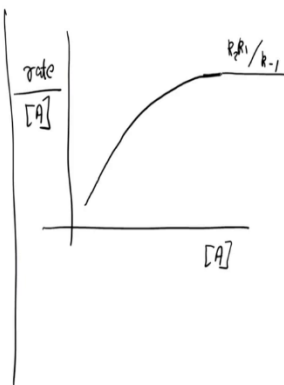
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The curious case of isomerization  
of cyclopropane

$$\frac{\text{rate}}{[A]} = \frac{k_2 k_1 [A]}{k_{-1}[A] + k_2}$$

$$[A] \text{ large: } k_{-1}[A] \gg k_2$$

$$= \frac{k_2 k_1 [A]}{k_{-1}[A]}$$



$$[A] \text{ small: } k_{-1}[A] \ll k_2$$

$$\frac{\text{rate}}{[A]} = \frac{k_2 k_1 [A]}{k_2}$$



So, remember in experimentalists were plotting rate divided by concentration of A, so I have just divided that and I get this equation now. And I want to make a plot of my prediction versus

concentration of A. Well, you can just use a computer to plot this but it's always fun to be able to plot this on your own, at least the qualitatively what it will look like.

So, we will think of this plot in 2 limits. 1, when A is very large, in that limit I will assume is  $\gg k_2$ , so that I will ignore  $k_2$  in the denominator, so in this limit I get something that is independent of A, so at large A I get a flat curve which  $= k_2 k_1 / k_{-1}$ .

Let us also look at the smaller limit when A is small such that  $k_1, k_{-1} * A \ll k_2$ . Then my rate over A will be  $= k_2 k_1 * A$  and in the denominator, I will ignore the first term and I will get simply  $k_2$ . So, here I will get something that is proportional to A. So, you get a curve that looks like this similar to the 1 that you get in experiment ok. So, experiment by the way does not matches exactly with this observation and you need to do a bit more to get the experimental result exactly right, but that is a story for another course.

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Summary – module 2

- Elementary reaction: Reactants combine directly to give products without any stable intermediate.
- For an elementary reaction  $aA + bB \rightarrow cC + dD$ :  
$$\text{rate} = k[A]^a[B]^b = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$
- Rate law equation
- Steady state hypothesis: intermediates concentration do not change with time

So, in summary what we have looked today, it is what is an elementary reaction, how to combine these elementary reactions to give a reaction mechanism and how to write rate law equations. And if you want to solve using the rate law equations, what is a net rate of a given complex reaction we use what is called a steady state hypothesis. So, we end here and we will move on to calculating rate constants as a function of temperature in the next module. Thank you.