Advanced Chemical Thermodynamic & Kinetics
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Lecture – 14
Review of Chemical Kinetics – I

Hello everyone. So, in this lecture, we will review some general aspects of Chemical Kinetics. Now, this topic or the discussions that I am going to cover can be found in any standard textbook on physical chemistry or in any textbook on chemical kinetics. The textbooks which are referred to you, these textbooks cover the entire portion, which I am going to discuss.

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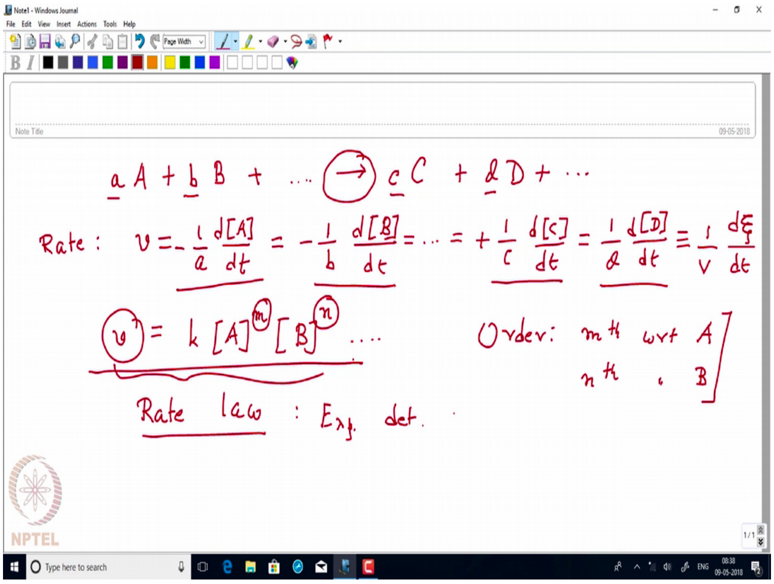

$$\underline{a}A + \underline{b}B + \ldots \boxed{\rightarrow} \underline{c}C + \underline{d}D + \cdots$$

$$\text{Rate}: \quad v = \underline{-\frac{1}{a}\frac{d[A]}{dt}} = \underline{-\frac{1}{b}\frac{d[B]}{dt}} = \ldots = \underline{+\frac{1}{c}\frac{d[C]}{dt}} = \underline{\frac{1}{d}\frac{d[D]}{dt}} \equiv \frac{1}{V}\frac{d\xi}{dt}$$

$$\underbrace{\boxed{v} = k[A]^{\boxed{m}}[B]^{\boxed{n}} \ldots}$$

Order: mth wrt A
nth " B

Rate law : Exp. det.

So, the first thing, we study in chemical kinetics is about the rates of the reactions. And then the first thing, we study is suppose we have a balanced chemical reaction, which I am writing in a most general way that I have some reactants, which are a and b, capital A and capital b, and they react together along with some other reactants. And then they produce some products, which are c and d, capital C and capital D, and maybe some other products. And the stoichiometries are given as small lowercase symbols like a, b, c, and d.

Now, these for this reaction, we can define the rate of the reaction, which can be expressed either in terms of the reactants or in terms of the products. Now, the rate is always expressed from the stoichiometric equation. And as you know that rate often, we call it as denote it as v, because v is basically the velocity of the reaction. And we write it, if I write it in terms of the reactant a, and write it as d A d t where the a inside the third bracket denotes the concentration of a, and then we have to divide by the stoichiometric number with a negative sign, because the negative sign is indicating that this is a reactant it is being consumed over time. So, the concentration of A is decreasing over time. The reason is we have actually chosen this reaction to be irreversible, because I have written it as a single arrow.

And we can we could also express it in terms of the other reactant b, so for that it will be 1 minus 1 over small b d concentration of B d t. Similarly, we could also write it in terms of the product concentrations. Now, remember that the products are actually growing in time, so instead of a minus sign, we will have a plus sign here. And I will have 1 over c d concentration of c dt, which is equivalent to also writing on over d concentration of d, and dt. So, all these terms are actually equivalent to the unit advancement of the reaction.

Now, advancement is or the progress of a reaction, we define, when we discuss the thermodynamics of reaction, how the Gibbs free energy changes. And you can go back, and look at your textbooks, which are recommended to you what is the meaning of advancement. And in this case, the overall rate of the reaction can be shown that this is the advancement per unit time per unit volume that is defined as the rate of the reaction.

Now, this is the overall how I can express the rate, but then experimentally the rate is found to vary with concentrations of the reactants, it can also vary with the concentration of the products in rare cases. Now, if we find this rate, which can be expressed as either of these terms like 1 over a d A d t or 1 over b d B, d t with the negative signs or in terms of the products, so that rate suppose we find it to be equal to some constant times the concentration of A raised to the powers let us take some number m; concentration of B raised to the power some number n; something like that. Then we tell that this equation which is basically the rate is equal to some expression in terms of the concentration that equation we call it as a rate law.

So, rate law is an experimentally determined quantity. So, rate laws, we cannot actually predict from the concentration I will come back from the stoichiometric equation, I will come back to this point once again. So, this is an experimentally determined quantity or we can just say it is basically experimentally determined equation.

Now, what are these numbers m and n? so this m and n are actually orders with respect to A and B. So, the order of the reaction means the number to which the concentration is raised to the power. So, for this reaction the way I have written it the order is mth order with respect to A; It is nth order with respect to B; again this mth order or nth order as I said it is coming from the rate law, which is experimentally determined quantity. So, order of a reaction is an experimentally determined quantity.

Now, order of reaction has a meaning, if and only if I can write this equation like this like, for example the way I have written it that A to the power m, and B to the power n there will be cases, where actually we cannot write the order of a reaction in such a nice and compact form since then in those cases the order of a reaction does not have any meaning.

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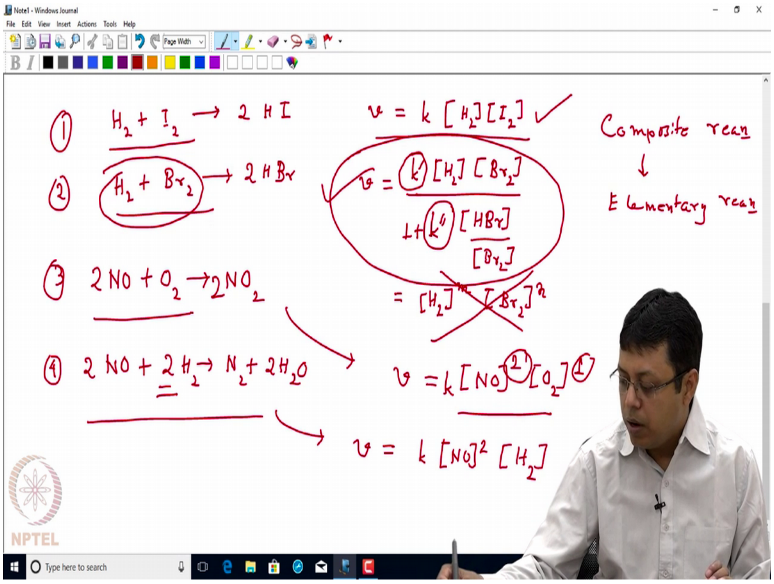

① $H_2 + I_2 \rightarrow 2HI$ $\qquad v = k[H_2][I_2]$ ✓

② $H_2 + Br_2 \rightarrow 2HBr$ $\qquad v = \dfrac{k'[H_2][Br_2]}{1 + k''\dfrac{[HBr]}{[Br_2]}}$

$= \cancel{[H_2]^m [Br_2]^n}$

Composite reaⁿ
↓
Elementary reaⁿ

③ $2NO + O_2 \rightarrow 2NO_2$ $\qquad v = k[NO]^{②}[O_2]^{①}$

④ $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ $\qquad v = k[NO]^2[H_2]$

Now, I will give you some examples of few specific reactions who after which you will have an over a clear idea, how basically the order of a reaction is has no connection with the stoichiometry rate or stoichiometric equation on the balanced chemical reaction. For example, for this reaction, say H 2 plus I 2 is giving 2 H I the order of a reaction or the rate law is found to be as some constant into which you call this constant, we call as rate constant into concentration of hydrogen into concentration of iodine.

Now, in this case as you see the rate law actually resembles the stoichiometric equation, but this is just accidental. In many cases, you will see that this it no way means that in the reaction the weight it was proceeding in that case hydrogen, and iodine molecules came together, and then they collided the overall collision at the rate, because rate is nothing but number of collisions per unit time, it is connected to that quantity.

So, the if I have actually the reaction rate governed by a process, where just the hydrogen molecules and the iodine molecules collided, then those number of collisions will be proportional to their product of the concentration terms. But, we cannot just simply say that since the order or the not the order the rate equation has a simple form like this, we cannot say that this reaction occurs via step, where hydrogen and hydrogen just colliding, and giving you the product. The reaction can have actually multiple states. So, most of the reactions, actually have many multiple steps in which some reactants first collide to give you something which is known as an intermediate. Then they intermediate again forms I mean collides with something else, and forms another intermediate, and then eventually it forms product.

So, any composite reaction, we can say is composed of many reactions many fundamental reaction, which cannot be divided further, and those fundamentally reactions we call it as elementary reactions. So, elementary reactions we will discuss more about it, but for the time being just remember that the elementary reactions are those reactions, which basically represent the most fundamental step of a reaction.

Now, as I said most of the reactions I am writing here are actually composite reactions. From the rate law, it may look that it is a it is an elementary reaction, but they are most of them are not. For example, I will give another example of this type hydrogen and the bromine reaction. Now, you see that this reaction is also very similar to the previous reaction it is hydrogen, and iodine this is instead of iodine it is hydrogen, and bromine.

Now, for this reaction, the rate law which is experimentally determined quantity is found to be a rate constant K prime into hydrogen concentration into a bromine concentration divided by another rate constant. So, it will be 1 plus another rate constant into H B R concentration divided by B r 2 concentration. Now, this reaction is very interesting.

Now, if you look at it carefully for this reaction, I cannot write the rate in terms of simple equation something like H 2 to the power m B r 2 to the power n something like that. So, for this reaction I since I cannot write it in this form, this reaction does not have any specific order. And also, you see this reaction has a multiple rate constant, it is not only just a one rate constant. So, this expression that the rate of the reaction is proportional to not proportional it is dependent on H 2, and we had 2 concentration. But, in a very complicated way was found experimental.

And once we find it then we propose a mechanism for this reaction, where we say that this reaction does not proceed like a collision between hydrogen and bromine molecules. But, rather it goes through our multiple steps, where the overall stoichiometry may look like that a hydrogen and bromine are reacting together, but there are many elementary steps involved. And then once we work on the kinetics of these elementary steps, we should at the end of the day be able to reproduce or predict the observed rate law.

Now, I will give you a few more examples just like we gave you the example of hydrogen and iodine to give you hydrogen iodide, there is also another example nitric oxide and oxygen giving you nitrogen dioxide for this reaction. The rate of the reaction is found to be some rate constant times nitric oxide square and oxygen.

Now, again you may have a notion that it is probably an elementary reaction, because as I see that the Stoichiometries are exactly appearing in the rate law also, because, two molecules of nitric oxide reacts it one molecule of oxygen giving two molecules of nitrogen dioxide. And they in the rate equation I find that the order is second order with respect to nitric oxide; and first order with respect to oxygen.

Now, again this is a wrong concept that the reason is what we are saying is two molecules of nitric oxide collides with one molecule of oxygen, and that kind of collision probability is very less. Because, collision probability for gas phase reaction are mostly by molecular probability of three body collision is very very rare. Because, you can remember that you can you can argue follow is that the probability of three bodies, simultaneously colliding into each other will be much much lower than the probability of two bodies colliding together. So, we exclude that possibility, and we say that although the overall order for this reaction is three. By overall order, we mean the some of the orders for individual reactants, and although the overall order is 3, this reaction is not a trimolecular elementary reaction it is composed of many reactions.

Now, a similar looking reaction, which is a nitric oxide reacts with hydrogen here, and to produce nitrogen and to 2 H 2 O for this reaction, we find that the rate is equal to nitric oxide squared, and then concentration of hydrogen. Now, here you see that although the in stoichiometry, there is number 2 in front of hydrogen, it does not appear in the rate law. So, you cannot predict anything about the rate of the reaction or the rate law will look like, and what is the order of the reaction, which is obtained from the from the rate law. You cannot predict from the stoichiometric equation, which is the balanced chemical reaction.

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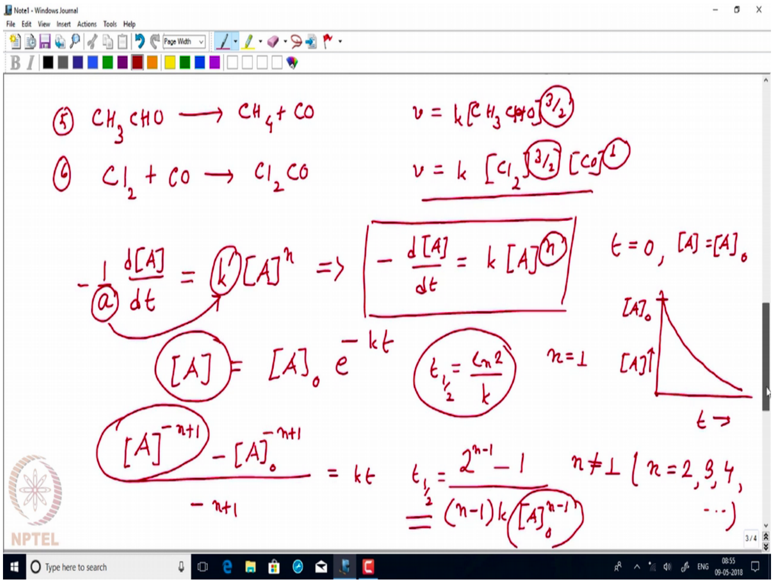

⑤ $CH_3CHO \longrightarrow CH_4 + CO$ $v = k[CH_3CHO]^{3/2}$

⑥ $Cl_2 + CO \longrightarrow Cl_2CO$ $v = k[Cl_2]^{3/2}[CO]^{1}$

$$-\frac{1}{a}\frac{d[A]}{dt} = k'[A]^n \Rightarrow \boxed{-\frac{d[A]}{dt} = k[A]^n}$$

$t = 0, [A] = [A]_0$

$$[A] = [A]_0 e^{-kt} \qquad t_{1/2} = \frac{\ln 2}{k} \qquad n = 1$$

$$\frac{[A]^{-n+1} - [A]_0^{-n+1}}{-n+1} = kt \qquad t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

$n \neq 1 \; (n = 2, 3, 4, \ldots)$

Now, we will give you one more two more examples, where you will see that how it is a very different, this rate law can be from if for a very very simple reaction. Now, the 5th example I have is the decomposition of acetaldehyde into methane and carbon monoxide. And again for this reaction the rate law is found to be some rate constant into acetaldehyde concentration raised to the power 3 by 2. Now, you can see that the rate law is now the order of the reaction is fractional. So, order of the reaction in this case is a unique example, where it is a fractional.

One more point I wanted to make here is that, when we talked about the hydrogen and bromine reaction in the previous example. So, you see that here the H B r also appears in the equation of the rate equation, which means the product can also influence the rate. Now, in this case, as you see the H B r appears in the denominator meanings as the H B r is forming. The rate of the reaction will be decreased, which means actually this is an example of inhibition, in sense that formation of the product can actually suppress the reaction.

I will give you one more example, which will be the last example of this kind, and this is also seemingly a very simple reaction that chlorine and carbon dioxide reacts to give you an adapt C l 2 C O, and that rate of the reaction was found to be chlorine raised to 3 by 2 into carbon monoxide. Now, you can see the complexity of the rate law, and it is fractional order with respect to chlorine; it is first order with respect to carbon dioxide. So, the bottom line again here, to discuss all these things is that, you cannot predict a priori anything about the order of the reaction or the rate law just by looking at the stoichiometric number.

Now, we will move on and we will talk about the integration of the rate law. Now, suppose I have a reaction again something like a general reaction, and I find experimentally that the rate of the reaction, which and for the time being let us say the 1 by a or we can actually keep the 1 by a. Suppose, it is found to be varying with nth power of A. Now, I can actually instead of writing it as 1 over a, this a can be absorbed into this rate constant. And I can actually rewrite it like this minus d A d t, which is the rate law, and our the expression for the rate, and the rate law is found to be some rate constant into A to the power n. Now, this is known as the differential rate law.

So, from a differential rate law, what we do is that, we integrate it. And when you do the integration all of you know that we need some limits of integration just to get rid of the constant of the integration. Now, in this process, we always say that at initial con the concentration, when a time was at 0, when the reaction was started; the amount of A was say A 0, we will denote it as A 0. So, A suffix 0 denotes the concentration of A at time 0. Now, if we can actually integrate it, and the integrations are you have already studied. I hope the integration of the rate law.

So, for if n is equal to 1, which is known as first order reaction, because it is raised to the power n, so the order of the reaction as I have written here inside the box is nth order. Now, if n is equal to 1, so the I can get a I can integrate this equation very readily, and I will get a 1st order rate expression. Now, also for how if I want to plot the 1st order X expression, it will be just an exponential decay with respect to time. So, from an initial concentration of A 0, the at any time A, actually decreases exponentially with respect to time.

Now, we can also define a quantity, which is known as the half life of the reaction, which is defined as the time taken for the reactant to fall to its half value of its initial concentration. Now, we can easily figure out. I we have to just put A to B A 0 by 2, and then we can solve it what is at what time that happens. And you will get it as natural log of 2 divided by the rate constant. Now, only for a 1st order reaction the half life is independent of the concentration.

Now, if you ask this question what happens for n not equal to 2, then the rate law looks like this. So, we will have say A raise to the power minus n plus 1. It is a very simple integration. And you can actually look up the textbooks that are recommended or you can also look up the YouTube videos for the course on Thermodynamics and Kinetics, or Introduction to Thermodynamics and Kinetics, and we will have A raise to minus n plus 1 and divided by minus n plus 1 is equal to k t.

Now, as you can see that for this reaction, this is a general reaction for n not equal to 2. For this reaction, if we calculate the half-life, so this half-life expression, well you can again calculate it. If instead of a you just put it as A 0 by 2, and naturally there will be a factor, which is 2 to the power n minus 1 minus 1 and, we will have n minus 1 into k into A 0 raised to power n minus 1.

Now, the point here is for any reaction, which is not a 1st order reaction, the half-life actually depends on the initial concentration A 0. For A 1st order reaction, only for A 1st order reaction the half-life is independent of the initial concentration no matter which concentration you start with the half-life will be independent. The examples are radioactive decay, which actually depends only on the concentration of the radioactive material present at any time and so it follows a 1st order rate law. And, we see that they are actually half-life is a very important quantity to tell about a particular species. And, we always say for example this isotope law of plutonium has this half-life, and that is the meaning of that.

But, for any other reaction, which is not a 1st order, where at not equal to 2 their half-life is directly connected to the initial concentration. So, it will matter what you will started doing. Now, as you see here most of the cases, we usually the textbook discuss about the

2nd order reaction, where n is n is basically this should be actually n not equal to 1. Say, for example if I take n equal to 2, so, n can be 2, 3, 4 or anything it can be also a fraction. Now, suppose if I take n equal to 2, then I can actually reduce this expression. As you can see it will be minus 2 plus 1, so it will be 1 over a something like that, and so I can reduce it. I can go to the next page, and I can just write it down there.

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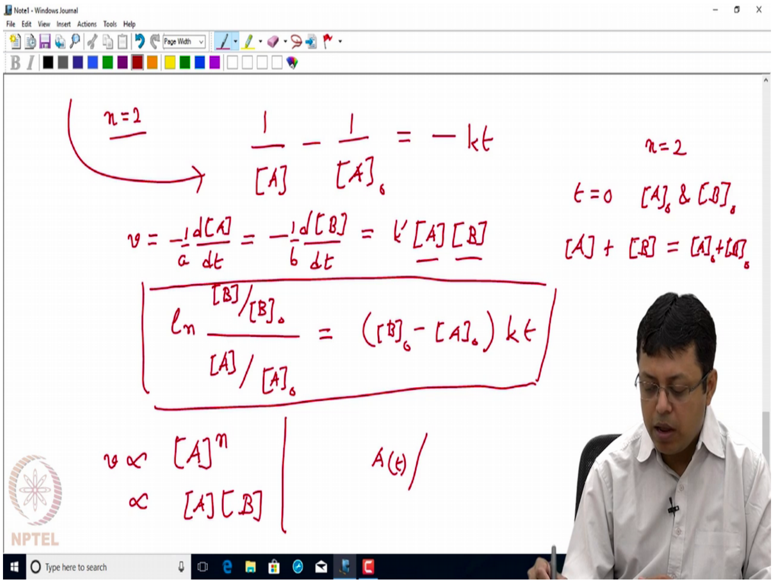

$n=2$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = -kt$$

$n=2$

$t=0 \quad [A]_0 \ \& \ [B]_0$

$[A] + [B] = [A]_0 + [B]_0$

$$v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = k'\underline{[A]}\,\underline{[B]}$$

$$\boxed{\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)kt}$$

$v \propto [A]^n$

$\propto [A][B]$

$A(t)/$

So, for any 2nd order reaction as you can see here, we can start from here. So, if n equal to 2, will get just follow this equation, what we are getting, we will get 1 over A minus 1 over A 0 is here, I will get minus 2 plus 1, which will give me a minus sign, so that will be minus k t. So, this expression, you have seen for a reaction, which is 2nd order.

Now, similarly we can also derive the rate law for any nth order, for example 3rd order reaction. Now, often this for a 2nd order reaction, may involve not just A square, but it can be actually 1st order with respect to 2 spaces. In the sense what I am saying is that the rate law, which I can write in terms of the concentration of or the decomposition of product A or the decomposition of product B. I am not writing the stoichiometric with let us write it stoichiometric, but eventually we can actually absorb the stoichiometric again in the rate constant.

And, then if it is found that the rate law is something like this, now actually it is different, it is not like a square, it is dependent on A and B. So, it is 1st order with respect to A, and 1st order with respect to B. But, the overall order is still 2, so which means, it is still the 2nd order reaction, but it is a slightly different 2nd order reaction. So, we can also integrate this 2nd order reaction, and what you will get the integrated rate law.

After you set the initial condition that at t equal to 0, the concentrations were A 0, and B 0. And also some stoichiometric balance that at any point, if I take the concentration of A and B together, that should be equivalent to their sum of initial concentration. If I apply those conditions, then I can actually integrate this equation using those initial condition as well as this mass balance. And what we get is something like this the integrated rate law, which will be l n b by b 0 divided by l n A by A 0 is nothing but equal to B 0 minus A 0 into k t.

Now, you see that moment we change the condition that I have in the rate law two spaces involved simultaneously. I will have a slightly more complicated expression for the integrated rate law. So, all these equations have been derived in the earlier course on in introduction to chemical kinetics and thermodynamics. So, I am giving you an overview to just to make sure that we can actually proceed with the basic concepts of chemical kinetics. Now, so far what we have discussed let me summarize that, we discussed what is the order of the reaction, and we emphasized this point again and again that the order of a reaction, which is an experimentally determined quantity has nothing to do with the stoichiometry of the reaction. You cannot a priori predict the order of a reaction just by looking at the stoichiometry of the reactions.

And, we gave you a few examples of real life examples how few a reactions what are the experimental I determined ordered, and we found that there is no correlation. Sometimes, you may accidentally get a correlation, but that does not mean that the reaction is proceeding by that particular pathway, which we will be discussing later.

And, then we gave you few specific examples like if the order is found to vary as A to the power n, and we gave you bases not the order the rate of the reaction is basically we found something like that or something like A into B, and we showed that for those cases, we can actually integrate the differential equation, which is the rate law in an integrated form, so that we can find actually the amount of A at any time or amount of B at any time. So, now we will be discussing about a few specific examples, which will be necessary for the subsequent discussion to understand the mechanism of chemical reaction.