Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 28
Chemical Kinetics: Rate laws – Part 1

So far, we have discussed the thermodynamics, from an equilibrium approach, in the sense that, we did not discuss the, rates of changes in a process. For example, we talked about chemical reactions and we talked about the, changes in free energy or the reaction Gibbs free energy when chemical reaction happens.

However we did not tell anything about how fast or how slow these react, start a reaction it reaches the equilibrium. Those things we will be discussing under chemical kinetics. So, which will start in today's lecture; now, to begin it, will give you an example how to, how you can quantify the rate of a reaction? Now, just take an example of a reaction.

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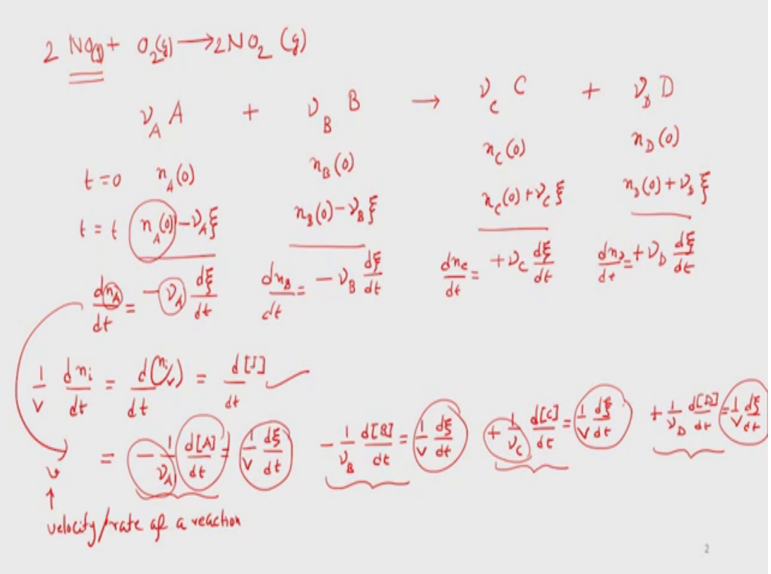

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$$

$t = 0$: $n_A(0)$, $n_B(0)$, $n_C(0)$, $n_D(0)$

$t = t$: $n_A(0) - \nu_A \xi$, $n_B(0) - \nu_B \xi$, $n_C(0) + \nu_C \xi$, $n_D(0) + \nu_D \xi$

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \qquad \frac{dn_B}{dt} = -\nu_B \frac{d\xi}{dt} \qquad \frac{dn_C}{dt} = +\nu_C \frac{d\xi}{dt} \qquad \frac{dn_D}{dt} = +\nu_D \frac{d\xi}{dt}$$

$$\frac{1}{V}\frac{dn_i}{dt} = \frac{d(n_i/V)}{dt} = \frac{d[I]}{dt}$$

$$v = -\frac{1}{\nu_A}\frac{d[A]}{dt} = \frac{1}{V}\frac{d\xi}{dt} \qquad -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{V}\frac{d\xi}{dt} \qquad +\frac{1}{\nu_C}\frac{d[C]}{dt} = \frac{1}{V}\frac{d\xi}{dt} \qquad +\frac{1}{\nu_D}\frac{d[D]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

For example, this nitric oxide oxidation; so, nitric oxide gets oxidized to nitrogen dioxide, this is a gas phase reaction, where all the species are in gas phase. So, this is also gas, this is also gas, and this is also gas, and then the question is, how will you describe the rate of the process?

Now, suppose I am describing the rate with respect to the nitric oxide molecule, and suppose per minute, 100 molecules of nitric oxide get consumed. So, I would say that the rate is minus 100 per minute. And then, if we monitor the concentration of oxygen, one will say, no, actually the rate is not minus 100 per minute, it is minus 50 per minute, because the rate is actually the stochiometry, if we see the reaction, it is basically 2 is to 1 for nitric oxide and oxygen, with respect to the nitrogen dioxide will say that, the rate is plus 100 per minute.

So, there is an inconsistency in the, in the description. So, in order to avert that, we want a, a quantity, which will take care of all these stiochiometric things inherently, and we already discussed what is this quantity. This quantity is known as the advancement of the reaction or the advancement of the extent of the reaction. Now, we can actually write down the equation for example, we will just write a very general equation like say, nu A of A plus nu B of B is going into nu C of C and plus nu D of D.

So, these are basically the stoichiometry coefficient, nu A nu B nu C and nu D. We talked about it, when we talked about the reaction quotient, under chemical equilibrium. Now suppose at time 0, the initial concentrations were, for nu A; it was nu A 0 nu at time 0. So, that we can or instead of not nu A, we have to write it as, something like n A, is 0, n A is the number of moles, not exactly the concentration. And similarly, we call it say it as, n B 0 and n C 0 and n D 0 for the number of moles for the species A B C and D.

Now, suppose at time t, the advancement of the reaction is xi. So, the amount of n A that will be left, will be nothing but, at some finite time will be n A at time 0 minus, there will be minus sign, because it is being concerned, minus nu A into xi, for n B, it will be n B 0, minus nu B into xi. Similarly for n C and n D, we can just write these equations, but there will be a plus sign because C and D and are products, and similarly for n D, we can write it like this. And then, we ask this question, what is the rate of change of this concentration? To ask that question, we can actually take the derivative of this each of these values with respect to time.

If we take the derivative, so then, we see that this part will be, will not be there, because this is just a constant. So, what we will have is, minus nu A d xi d t minus nu B d xi d t. Here will have plus nu C d xi d t, and here we will have plus nu D d xi d t. Now usually, this nu A, this we are basically calling as a, how much the reaction has changed or how much the reaction has been proceeded.

So, that is basically the change in the reaction. So, this is nothing but the, rate of change of species A, this is nothing but, the rate of change of species B, this is nothing but the rate of change of species C, and this is also nothing but the rate of change of species D. Now you see here, that usually, we can actually, instead of writing it as n A, the more relevant quantity will be to consider concentration, the reason is suppose you are doing working with a big vessel, and now you can actually experiment on a particular volume, and if I twice the volume, then you will see that the number of n A that has changed will also increase or decreased by twice amount.

So, there again we will have an inconsistency. So, better actually, we can divide it by the volume, and just look at the concentration, because that will be independent on the amount of the substance you are, you are observing. So, we can actually divide both side by the volume, and instead of writing 1 over V d n i d t, where i is some species, which can be a b c or d, we can actually write it as, d t of n i by V, or we can just write it as d d t of the concentration of i, that we can always write. And also, the next step, what I am going to do, I am going to divide by 1 over the volume, and use this relation, plus I am also bringing down, the stochiometry coefficient, with the sign on the left side.

So, what we will get is that, we will see minus 1 over nu A, if I divide in the volume on left hand side, it will be d A d t, that will be nothing but, 1 over V d xi d t, for the species B it will be minus 1 over nu B, d b d t will be nothing but, 1 over V d xi d t, for species C it will be plus one over nu C d c d t will be nothing but, 1 over V d xi d t, and for species D it will be plus 1 over nu D, d of D d t is equal to 1 over V d xi d t.

Now, we see a very beautiful thing that all these equations, now are equal to the same value, which is the advancement of a dye reaction and per unit volume.

That we call as the velocity of the reaction or the rate of the reaction. So, it is called as velocity or rate of a reaction. So, the reaction rate can be expressed in terms of either a, which is a reactant, or b which is also a reactant, or c or d which are actually products. And every time we are writing it, we are basically writing, the rate of change of that particular species and divided by the stoichiometric coefficient.

Now, the stoichiometric coefficient contains a negative sign, if it is a reactant, and it is it is a positive number, if it is a product ah.

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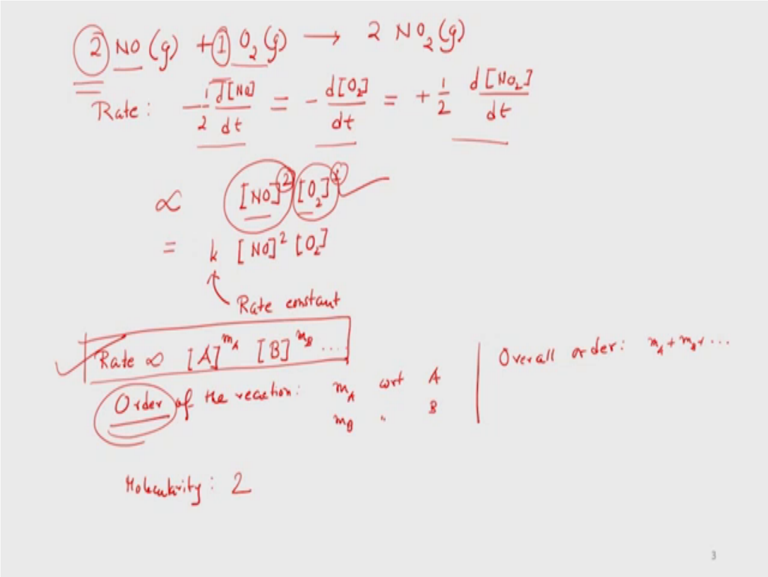

$$\boxed{2} NO(g) + \boxed{1} O_2(g) \longrightarrow 2 NO_2(g)$$

$$\text{Rate}: -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt}$$

$$\propto [NO]^{2}[O_2]^{1}$$

$$= k\,[NO]^2[O_2]$$

$$\uparrow \text{Rate constant}$$

$$\boxed{\text{Rate} \propto [A]^{m_A}[B]^{m_B}\ldots}$$

Order of the reaction: m_A wrt A, m_B " B

Overall order: $m_A + m_B + \ldots$

Molecularity: 2

So, coming back to the example which we just gave 2 nitrogen, nitric oxide, 2 molecules of nitric oxide reacts with, 1 molecule of oxygen, to give you 2 molecules of nitrogen dioxide. So, that the rate of the reaction, we can write it as, the velocity of the reaction in terms of reactant, in terms of nitric oxide it will be minus half d no d t, in terms of oxygen it will be minus 1, it is basically minus 1 by 1 d o 2 by d t and this will be plus half d no 2 by d t.

So, this is basically the expression for the rate. Now the question is, we will do some experiment, and then we will try to understand, what this rate, which is expressed either in terms of the reactants or in terms of the product, what this rate is equal to, equal to what? How it varies with the concentration of the reactants of the products?

For this particular reaction, will see that this rate, which can be expressed in one of these terms, is equal to, or it varies actually with a concentration of a squared concentration of a N O, and it varies linearly with the concentration of oxygen.

So, together we can write it that the concentration varies with N O square and oxygen, and the proportionality constant, we call it as a rate constant. Now, when we can write a equation on the rate law in this form, in this form in the sense that, when suppose we have our rate, which we can write in terms of the concentrations of the reactants or the products raised to some number say m A, say it is proportional to A to the concentration of A raised to m A, or concentration of B raised to m B, something like that. Then we say that, the order of the reaction, is m A with respect to A, or m B with respect to B. And we can also talk about the overall order, overall order in the sense that, it will be the sum over all, all these numbers like m A plus m B plus all these things.

But, remember that the order of the reaction has a meaning only when, we can express the rate like this, but again remember that, these expression we got, only can, only get from experiments. This has nothing to do with theory, it is an experimentally determined quantity. So, and, and the order has a meaning only when, the rate can be expressed in terms of some proportionality, some, it is proportional to the concentrations of the reactants, and then only the order has a meaning. Sometimes we also talked about, the molecularity of a reaction. In the sense that, in this case, if we find that it is dependent on both nitric oxide and oxygen, then the molecularity of this reaction is basically 2, because 2 molecules are involved.

Now, the second thing I would like to point here is that, for this reaction, it is basically second order with respect to nitric oxide, it is a first order with respect to oxygen. Now the stoichiometry of the reaction is 2 N O and O 2. And we are also saying that, the rate of the reaction is a N O square and O 2, but this square, it has nothing to do with this 2, and this to the power 1, has nothing to do with this 1 here, because the stoichiometry has nothing to do with the rate law.

The rate law can be very very complicated. So, here it is by chance we got that, it is happening as N O square and it is happening as oxygen. Let me give you some example.

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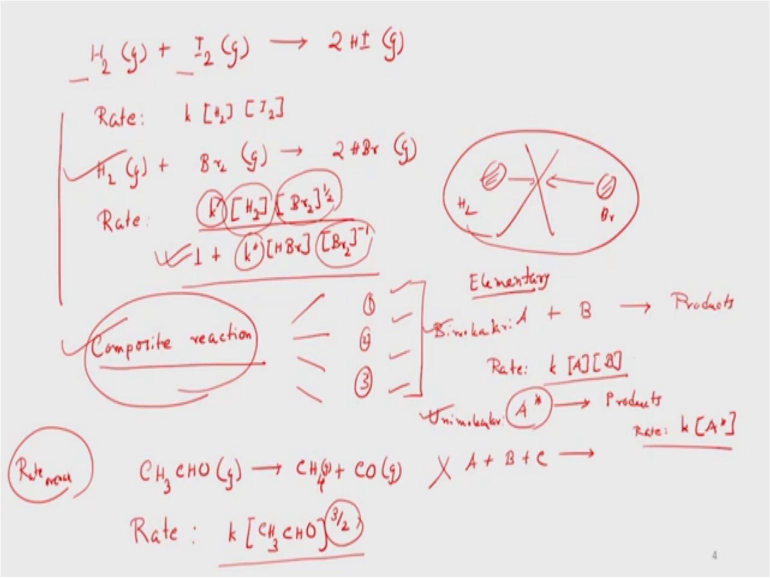

Let us consider a very simple reaction. So, let us say 2, we can actually first give you the example of say, H 2 O 2 or H 2 gas plus iodine gas, to give you 2 H I. This is also in gas phase reaction of the production of hydrogen iodide, from it is constituent hydrogen and iodine. And the rate was found to be, I am saying that it is, it is found to be, meaning it is experimentally determined quantity, it is as simple as k into H 2 into I 2, which again you might think that, ok, the rate is just H 2 into I 2.

Because actually there is one molecule here, and one molecule here. Which is not true, because I will give you another example, H 2 and bromine gas, to give you 2 H B R, and the rate of that reaction is, it will be something like this, concentration of hydrogen, concentration of bromine to the power half, divided by one plus k double prime H B R to be a 2 minus 1.

Now, you see that the rate expression is fairly, fairly complicated. It is not simply proportional to rate concentration of hydrogen and concentration of bromine. And also here, you cannot say the rate is first order with respect to hydrogen, because it is not simply proportional to H 2, there are other factors also in the denominator. And you can also not say that, constant, the overall rate of the reaction is a half, or the order of the reaction is half with respect to bromine, or minus 1 with respect to bromine, or it is minus half with respect to bromine, you cannot say that. And also you see that, there are 2 rate constants actually for this reaction.

So, which readily hints, that the reaction does not happen like, I have 1 H 2 molecule and I have one B r 2 molecule, and they just collide with each other, and then we get a reaction, it does not proceed via that channel, it should have proceeded by a very very different channel. So, that means actually, this reaction is not happening via this mechanism, but via different steps which we call as elementary reaction.

So, all these reactions which we are considering are called composite reaction, in the sense that, they are composed of many many reactions, which are elementary or very fundamental reactions. So, where actually the 2 components come and hit or collide against each other, and then they form some intermediate species, and then intermediate species further react. So, it is some other component to give you the reaction.

So, any composite reaction can be decomposed into, many many elementary reaction, and if we add up, I will get the composite reaction. And if we find, now the rate law for each of the elementary reaction, then we can actually, we should get back, the composite reactions or the observed rate law. So, that will see for this particular reaction, the hydrogenation, hydrogen and bromine reaction to produce a H B R in gas phase.

Now, for a composite reaction suppose, or for an elementary reaction, suppose we have this condition, already we, we talked about it, that a composite reaction can be thought of, made of an, many elementary reaction. Now elementary reactions are usually bimolecular or unimolecular, and when you write elementary reaction, which means, this is the ultimate step where A and B are colliding to give something.

So, there we can write, the rate of that particular step for the elementary reaction as k into A into B. So, always for elementary reactions we can write it, and elementary reactions that always bimolecular or unimolecular in nature, unimolecular in the sense, you could have also some molecule going into the product, but of course, this molecule is already energized, that is what you are writing it as A star, and it may actually come from a collision, with another molecule, to give the product, how, come all of a sudden the molecule got energized, it, it may energized it by collision the bimolecular collision.

Three body collisions like this process A plus B plus C are extremely rare. We will just would not consider it. So, will not say that, this kind of elementary reaction exist. So, elementary reactions, we will always say that it is either bimolecular, or it is unimolecular. So, we will be discussing about unimolecular and bimolecular elementary reactions. So, any reaction can be actually decomposed into a set up bimolecular and unimolecular reactions, for which we can rate constant like this, and for the unimolecular reaction the rate will be nothing but, some rate constant into A star, something like this. And then, when we manipulate all this reaction, in all these elementary reactions, and if we try to calculate the rate constant for the overall reaction, or, or the, rate of the overall reaction.

So, the rate of the overall reaction should match the observed rate, which we experimentally observe, we cannot do it, I mean, I have been show way, I mean, we have to do some experiment to get the rate constant or the rate law. And once our proposed model that so, this composite reaction is composed of these 1 2 3 elementary steps, and it successfully matches the observed rate law, when we combine all of them, then this mechanism which we proposed, is acceptable. But there could be actually, many mechanisms for the same reaction and it, you may have a situation that one or more, may be acceptable mechanism. For that we have to look at the intermediates, and then, to establish that the mechanism you are proposing is the correct one, not the other mechanism which is correct one.

So, those things we will be discussing, when we discuss the, mechanism of a reaction. To give you another example of a very simple little reaction, we know that acetaldehyde decomposes into methane and carbon monoxide. And the rate of the reaction, again it is an experimentally determined quantity, and it was found to be some rate constant times the concentration of acetaldehyde raised to the power 3 by 2.

Now, you say that this has an order, but this order is fractional order it is 3 by 2. So, it is very very interesting, that you might, in most of the cases actually, you want a, for a composite reaction, you will not get the order, simply as the way we had written that, it. It will be something like, the A to the power m A, B to the power m B, something like that, only when you can write it, then only the order of a reaction has a meaning, or a composite reaction has a meaning otherwise it does not have any meaning.

So, in the next part, we will be discussing on the rate of the reaction, and then we will say that, if the rate is found to be say first order, or if the rate is found to be second order, how will you express the rate law? And how we can get from a differential expression? Because remember that, we wrote everything in terms of a differential expression, like,

like this equation or this equation, but instead of a differential expression, we need an integral expression, in the sense that, we do not want it in the differential notation or the derivative notation, we want a concentration of say, nitric oxide at a particular time, how it varies with time? For that we have to integrate the differential rate law, and get an integrated version of the rate law. And will be first discussing, how one can get the integrated version of the rate law, starting from a differential version, and then we will talk about the mechanism.

So, we will pick up few examples and, and then we will say that, how a mechanism can be proposed, which can satisfactorily explain the observed rate law of this particular reaction.

Thank you.