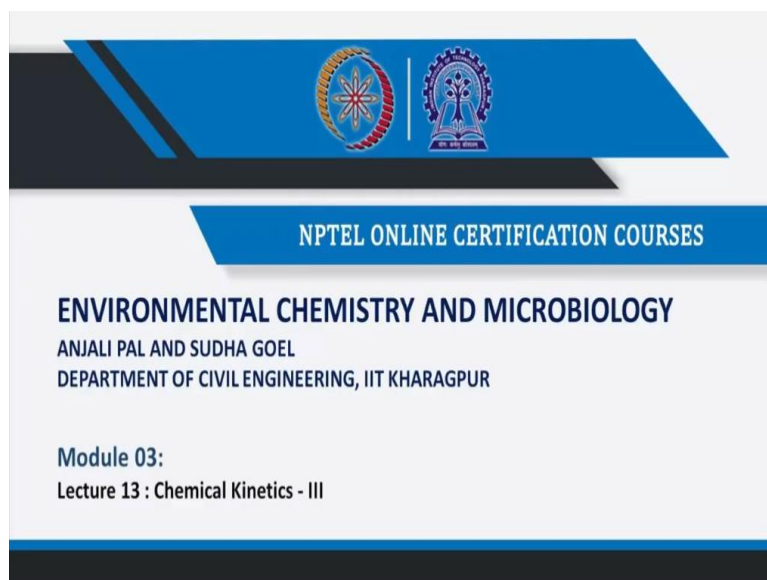


Environmental Chemistry and Microbiology
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Module - 3
Lecture - 13
Chemical Kinetics - III

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are both from the Department of Civil Engineering of IIT Kharagpur. We have divided this course into 2 parts. The first part, Environmental Chemistry will be covered by me and the second part, Environmental Microbiology will be taught by Professor Sudha Goel. So, this is my module 3 and this is my thirteenth lecture.

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In Module 3, I am discussing chemical kinetics.

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Chemical Kinetics

- Zero order reaction
- First order reaction
- Second order reaction
- Integrated rate law

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In this lecture, I will be covering the zero-order reaction, first order reaction, second order reaction and integrated rate law. I have already discussed about the rate of a reaction, the order and rate constants and the differential rate laws and how we can apply differential rate laws to find out the order in the previous lectures.

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Zero order reaction

Consider the conversion of a single reactant to a single product

A (reactant) → P (product)

If such a reaction follows zero order kinetics, then the rate of reaction of A is expressed by the rate equation

Rate = $-dC_A / dt = k (C_A)^n$ (n is the order of reaction)

Or, Rate = $-dC_A / dt = k (C_A)^0 = k$
 Where k is the rate constant (or specific rate constant)

For zero order reactions the rate is independent of the concentration of reactant.

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Here, I will go into details about the integrated rate laws. Say for example, if we consider this reaction (1),



It is a simple reaction, where A is the reactant and P is the product. Say for example, this reaction is following zero order kinetics. Then, from the rate expression, we can tell that the rate is expressed as follows:

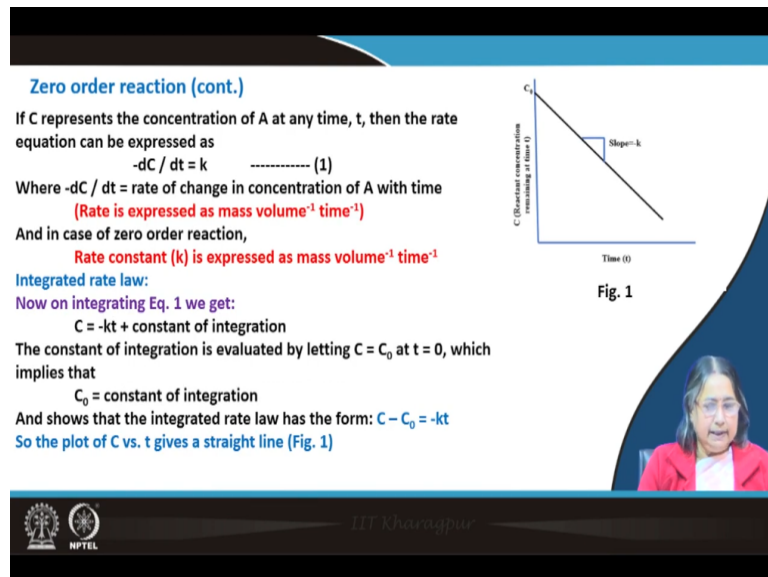
Rate = $-dC_A/dt = k(C_A)^n$ (n is the order of the reaction) $\dots \dots \dots (2)$

This is the rate law or rate expression. As it is a zero-order reaction, so we can write:

$$\text{Rate} = -dC_A/dt = k(C_A)^0 = k \dots\dots\dots(3)$$

So, it is k. So, from here, we can tell that zero order reactions, the rate is independent of the concentration of the reactant and, here k is the rate constant (specific rate constant). That, I already discussed in the previous lecture.

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Zero order reaction (cont.)

If C represents the concentration of A at any time, t, then the rate equation can be expressed as

$$-dC / dt = k \dots\dots\dots (1)$$

Where $-dC / dt =$ rate of change in concentration of A with time
(Rate is expressed as mass volume⁻¹ time⁻¹)

And in case of zero order reaction,
Rate constant (k) is expressed as mass volume⁻¹ time⁻¹

Integrated rate law:
Now on integrating Eq. 1 we get:
 $C = -kt + \text{constant of integration}$
The constant of integration is evaluated by letting $C = C_0$ at $t = 0$, which implies that
 $C_0 = \text{constant of integration}$
And shows that the integrated rate law has the form: $C - C_0 = -kt$
So the plot of C vs. t gives a straight line (Fig. 1)

Fig. 1

The figure shows a graph of Concentration (C) versus Time (t). The y-axis is labeled 'C (Reactant concentration remaining at time t)' and the x-axis is labeled 'Time (t)'. A straight line starts at a point on the y-axis labeled 'C₀' and slopes downwards. A right-angled triangle is drawn below the line to indicate its slope, which is labeled 'Slope = -k'. In the bottom right corner of the slide, there is a small video inset showing a woman with glasses and a red jacket.

In order to make it simplified, I will use dC/dt instead of dC_A/dt.

So, we have seen from the previous, in the previous slide that the rate is - dC/dt is nothing but k. This is for the zero-order reaction. I told already that rate always will be expressed in terms of mass per volume per time. And it is up to you that what units you will use for mass, volume and time. But for the zero-order reaction, the rate constant is the same as the rate. So, for zero order reaction, rate constant is expressed as the same like the same unit as we express for rate.

Now let us see the integrated rate law. It is easier than the differential rate law to visualise and to apply. Integrating equation (3),

$$C = -kt + \text{constant of integration} \dots\dots\dots(4)$$

Constant of integration can be found out by implying boundary condition that at time, t=0, C=C₀. From the boundary condition, constant of integration is coming C₀. So,

$$C - C_0 = -kt \dots\dots\dots(5)$$

Plot of C vs t will give a straight line where the y-intercept will give the concentration at t = 0, i.e., C₀.

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First order reaction

If we consider a reaction

A (reactant) → P (product)

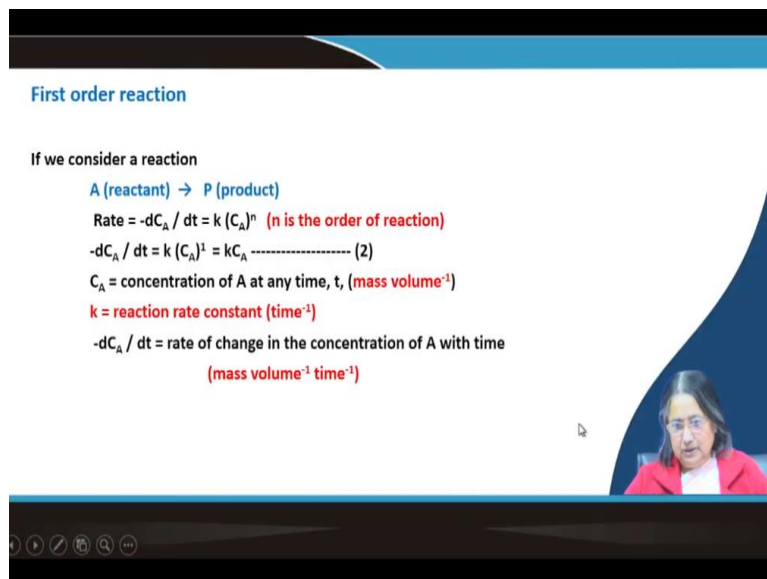
Rate = $-dC_A / dt = k (C_A)^n$ (n is the order of reaction)

$-dC_A / dt = k (C_A)^1 = kC_A$ (2)

C_A = concentration of A at any time, t, (mass volume⁻¹)

k = reaction rate constant (time⁻¹)

$-dC_A / dt$ = rate of change in the concentration of A with time
(mass volume⁻¹ time⁻¹)



Experimentally we will start the reaction, we will determine the concentration at different times. Then, we will just plot concentration versus t. Then we will see whether it is following a linear plot or it is not following a linear plot.

Now, let us see the case of first order reaction:

Writing rate expression:

$$\text{Rate} = -dC_A/dt = k(C_A)^n \text{ (n is the order of the reaction)(2)}$$

For first order reaction, n = 1

$$\text{So, rate} = -dC_A/dt = kC_A$$

where C_A is the concentration of A at any time t.

In case of first order reaction, k is the reaction rate constant which is nothing but the time inverse. This is very important to remember for first order reactions.

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First order reaction (cont.)

$$-dC_A / dt = k (C_A)^1 = kC_A \text{ ----- (2)}$$

First order reactions proceed at a rate directly proportional to the concentration of reactant.

➤ Since the rate of the reaction depends on the concentration of the reactant and the concentration of the reactant changes with time, so an arithmetic plot of the variation in the concentration of the reactant with time does not give a linear response (Fig. 2).

Integrated rate law:

➤ On integrating Eq. 2 and considering $C = C_0$ at $t = 0$ we get an integrated rate law of the form

$$\ln (C_0 / C) = kt$$

Or, $\log (C_0 / C) = kt / 2.3 \text{ ----- (3)}$

Eq. 3 suggests that a plot of $\log C$ vs. time for a first-order reaction will give a linear plot as shown in Fig. 3.

Now, from the rate expression of first order reaction, you can see that first order reaction proceed at a rate directly proportional to the concentration of the reactant. Since the rate of the reaction depends on the concentration of the reactant and the concentration of the reactant changes with time. Rate of the reaction depends on the concentration of the reactant and reactant concentration is changing with time. So, an arithmetic plot of the variation in the concentration of the reactant with time does not give a linear response. The curve will be like that as shown in Fig. 2 of the last slide. Slope at any point will be given by $-dC_A/dt$ (with minus sign, because it is the reagent). Now, if we apply the integrated rate law, then on integrating equation (2),

$$\ln(C_0/C) = kt$$

$$\text{or, } \log(C_0/C) = kt/2.303 \dots \dots \dots (6)$$

If you plot $\log C$ versus t , then you will get a straight line with negative slope, because it is the reactant. So, it will decrease with respect to time and the cutting point will be nothing but C_0 . But if you plot $\ln(C_0/C)$ vs time, then you will get a straight line with positive slope.

Now, previously we have seen that, for the zero-order reaction, we have seen that concentration versus time, will give you a straight line. But in case of first order reaction, you will see that $\log C$ or $\ln C$ versus time will give you a straight-line curve. This is the difference between the zero order and first order reactions.

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First order reaction

Half life
 Let us consider the first order gas-phase reaction

$$\text{N}_2\text{O}_5(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$$

$$\text{Rate} = -\Delta [\text{N}_2\text{O}_5] / \Delta t = k [\text{N}_2\text{O}_5]$$

$$\ln (C_0 / C) = kt$$

For first-order reaction the **half-life ($t_{1/2}$)** is very useful. The **half-life** is the time it takes for the concentration (C_0) of a reactant to fall to one half of its original value. That is, the final concentration is obviously $C_0 / 2$. So we can rewrite

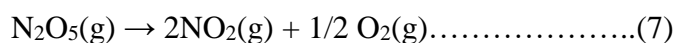
$$\ln C - \ln C_0 = -kt$$

 or,
$$\ln (C_0 / C) = kt$$

 or,
$$\ln 2 = kt_{1/2}$$

 or,
$$0.693 / t_{1/2} = k$$

Instead of denoting reactants and product by A and P an example of a real reaction is shown here (4):



This is a gas phase reaction and rate is given by:

$$\text{Rate} = -\Delta[\text{N}_2\text{O}_5]/\Delta t = k[\text{N}_2\text{O}_5] \dots \dots \dots (8)$$

Instead of writing $[\text{N}_2\text{O}_5]$, denoting concentration by C, for first order reaction

$$\ln(C_0/C) = kt \text{ (as explained already) } \dots \dots \dots (6)$$

Now, if you plot $\ln(C_0/C)$ against time, then you will get a straight-line curve, because it is a first order reaction. Let me explain here. Experimentally it has been determined, as a first order reaction. At the same time, you can see that the molecularity is also 1. If you can recall, I told you that the reactions can be thought in two different ways; one is the molecularity another is the order. So, in this case, if you see, the molecularity is 1, because only 1 molecule of N_2O_5 is involved in the balance reaction. Here it is matching with the order. But it may vary also. That you must remember.

Now, one thing is very important for the first order reactions. What is that? It is the concept of half-life. This is also very important for radioactive elements. All the radioactive elements decay by in first order. That is why, the radioactive elements are also characterised in terms of their half-life. So, half-life is very important for the first order reactions.

Half-life is always expressed in terms of $t_{1/2}$. So, what is half-life? Let the original concentration of radioactive element or reactant be C. Half-life is the time that will be taken for that reactant or for radioactive element to come to its half-concentration. Means, if you

start with C, then how much time it will take to come to C/2. That time period is known as half-life. So, in case of first order reaction:

$$\ln C - \ln C_0 = -kt$$

$$\text{or, } \ln(C_0/C) = kt$$

$$\text{When } t = t_{1/2}, C = C_0/2$$

$$\text{or, } \ln 2 = kt_{1/2}$$

$$\text{or, } 0.693/t_{1/2} = k \dots \dots \dots (9)$$

But there is no concentration term present in the expression of $t_{1/2}$. That means, half-life does not depend on the concentration. It is a very characteristic thing.

When I will discuss about radioactivity, then you will see that for a particular radioactive element (say for example Uranium), a particular half-life is there. It does not depend on the initial concentration as it is a characteristic thing. Now, you look into the curve ($[N_2O_5]$ vs time) in the last slide. So, if you start with 1 (y axis), then the half-life will be that time that taken to come to 0.5 (y axis). So, to come to this concentration (0.5), $t_{1/2}$ time is taken. Now you start with 0.5. So, half of 0.5 is 0.25. So, how much time it will take to come to 0.25? If you see the picture in the last slide, you will find that it corresponds to time $2t_{1/2}$. Similarly, when you start with 0.25, then, half of this is 0.125. So, total time taken to reach 0.125 is $3t_{1/2}$. So, like this, it will continue. And it is first order type curve (as shown in last slide).

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Second order reaction

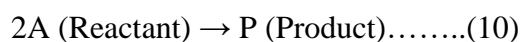
Let us consider a second-order reaction
 $2A$ (reactant) \rightarrow P (product)
 Rate = $-dC_A / dt = k (C_A)^2$
 k = reaction rate constant, $\text{mass}^{-1} \text{ volume time}^{-1}$

The integrated rate law for a second-order reaction has the form
 $(1 / C) - (1 / C_0) = kt$ -----(3)

An arithmetic plot of $1/C$ vs. time will give a linear trace, the slope of which is the k

Q.1. For a reaction such as
 A (reactant) + $2B \rightarrow P$ (product)
 Rate = $-dC_A / dt = \text{?????}$
 Will it be a first-order, second-order (or something else) reaction?
 How to express??

Now, let us come to the second order reaction. Second order reaction is also very common. Many reactions are second order reactions. Let us consider a second order reaction:



A is the reactant; P is the product. It is a second order reaction. So here, molecularity is also

2. So, by chance, molecularity and order is same here.

So, rate expression can be written as:

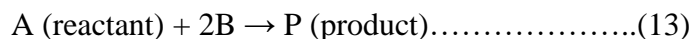
$$\text{Rate} = -dCA/dt = k(CA)^2 \dots\dots\dots(11)$$

Now, the integrated rate law for the second order reaction can be written as follows:

$$(1/C) - (1/C_0) = kt \dots\dots\dots(12)$$

So, plot of $1/C$ vs t will give a straight line with slope equal to k . So, for a second order reaction, if you plot $1/C$, here in the y axis and time in the x axis, then you will get a straight-line curve with positive slope. The cutting point is $1/C_0$. So, in the first order rate, you have seen, we have to plot $\ln C$ or $\log C$ versus time, to get a linear curve. In case of zero order C versus t to get a linear curve. In case of second order reaction, you have to plot $1/C$ versus t , to get a straight-line curve. So, it is a very simple method to get to know the order of the reaction, because you have the data set. At different time intervals, you have collected some samples for a reaction and you have measured the concentration of that particular reactant or product, whatever maybe. And then, you make a table. And then, after making the table, you just plot it. You have to make different plots. And then you will see which one is following the straight-line curve. Accordingly, you can decide what is the order of the reaction.

Let us consider a reaction involving two reactants as follows:



So, the stoichiometric ratio of A and B in the above reaction (13) is 1:2.

If this is the case, then how will you tell about the rate? What will be the order? Whether you will determine in terms of A or B or both, that is to be determined. It is so because, for some reactions you may just consider A and you can tell that this reaction is first order with respect to A. You can also say that this reaction is second order with respect to B. Or, you can tell that, overall order of the reaction is 3. So, how will you tell it? That is very important.

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Rates that depend on two or more concentrations

□ In many cases the rate of a reaction depends on the concentrations of two or more different chemical species. For example:


$$\text{rate} = k (C_A)^m (C_B)^n$$

- Here m and n do not come from the coefficients of the balanced equation. They should be determined experimentally.
- From the above rate expression we can say that, the reaction is mth order in A and nth order in B, and the overall reaction order is m+n
- As for a typical experiment:

$$\text{H}_2\text{PO}_2^- (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{HPO}_3^{2-} (\text{aq}) + \text{H}_2 (\text{g})$$
 In this case we observe

$$\text{Rate} = k [\text{H}_2\text{PO}_2^-] [\text{OH}^-]^2$$

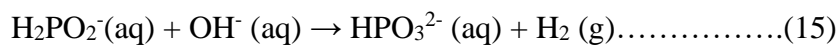
We can say that the above reaction is first order in $\text{H}_2\text{PO}_2^- (\text{aq})$ and second order in $\text{OH}^- (\text{aq})$. The overall order is 3. Accordingly the unit of k can be found out.



In many cases the rate of a reaction depends on the concentration of two or more species as follows:

$$\text{rate} = k(C_A)^m(C_B)^n \dots \dots \dots (14)$$

The 'm' and 'n' in the above equation (14) does not come from the balanced equation but determined experimentally. The reaction is mth order in A, nth order in B and therefore the overall order of the reaction is m + n. Let us give a typical example:



The rate of the reaction (12) can be expressed as:


$$\text{Rate} = k[\text{H}_2\text{PO}_2^-][\text{OH}^-]^2 \dots \dots \dots (16)$$

The reaction is first order in $[\text{H}_2\text{PO}_2^-] (\text{aq})$ and second order in $\text{OH}^- (\text{aq})$ and therefore overall order is 3.

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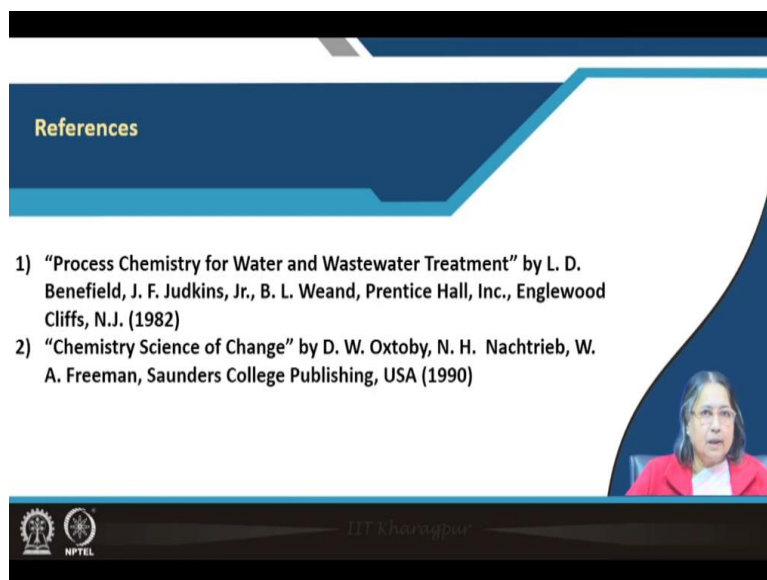
Then how to know the order of a reaction in a real experiment ????

- In a real experimental study we do not know before we start what the order of the reaction will be.
- In that case we have try several plots to find the best fit of the data and know the order of the reaction.



In real experiment, we do not know what is the order and we cannot speculate also. So, how we will determine the order? In that case, we have to take the experimental data. After that, we have to try different plots (zero-order plot, first order plot, second order plot). After that, depending on the which one is the best fit you can tell order of the reaction.

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References

- 1) "Process Chemistry for Water and Wastewater Treatment" by L. D. Benefield, J. F. Judkins, Jr., B. L. Weand, Prentice Hall, Inc., Englewood Cliffs, N.J. (1982)
- 2) "Chemistry Science of Change" by D. W. Oxtoby, N. H. Nachtrieb, W. A. Freeman, Saunders College Publishing, USA (1990)

The slide features a dark blue header with the word "References" in yellow. Below the header, two references are listed in black text. In the bottom right corner, there is a small video inset showing a woman with grey hair wearing a red jacket. At the bottom of the slide, there are logos for IIT Kharagpur and NPTEL on the left, and the text "IIT Kharagpur" in the center.

So, I have discussed integrated rate law, differential rate law and how to determine the order in this lecture. You can get from the same book that I already have mentioned in previous lectures. Thank you very much.