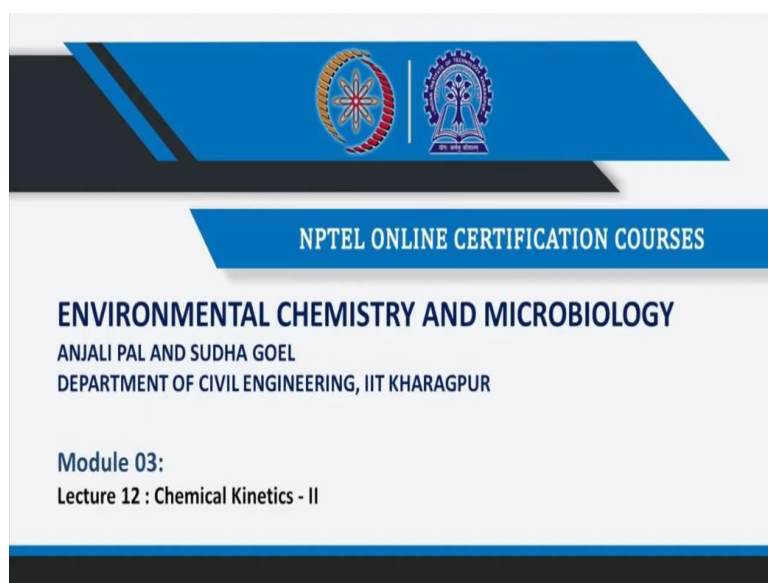


Environmental Chemistry and Microbiology
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Module - 3
Lecture - 12
Chemical Kinetics - II

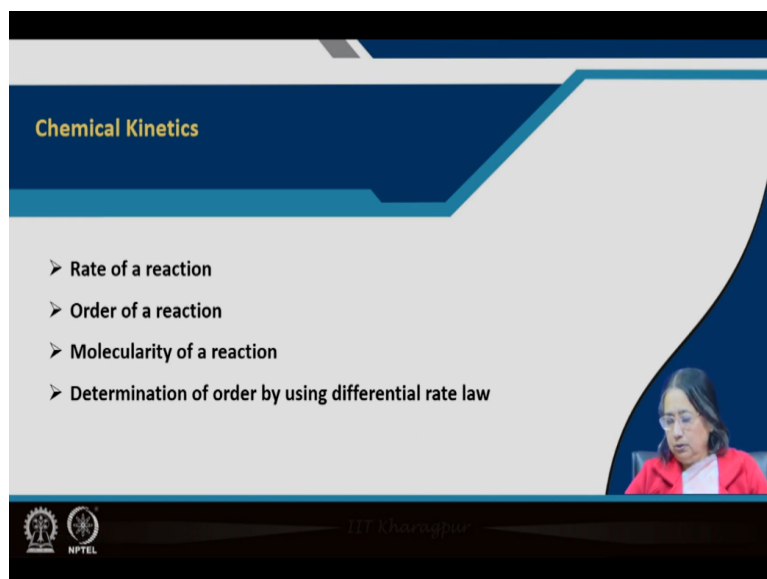
Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are both from the Civil Engineering Department of IIT Kharagpur. We have divided this course into 2 parts. The first part will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

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In my first module, I already told about the acids, bases and in my second module, I have covered the chemical equilibrium. This is my third module and I will talk here about the chemical kinetics. You all know that in chemical reactions there are some reactants that react to form some products.

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Chemical Kinetics

- Rate of a reaction
- Order of a reaction
- Molecularity of a reaction
- Determination of order by using differential rate law

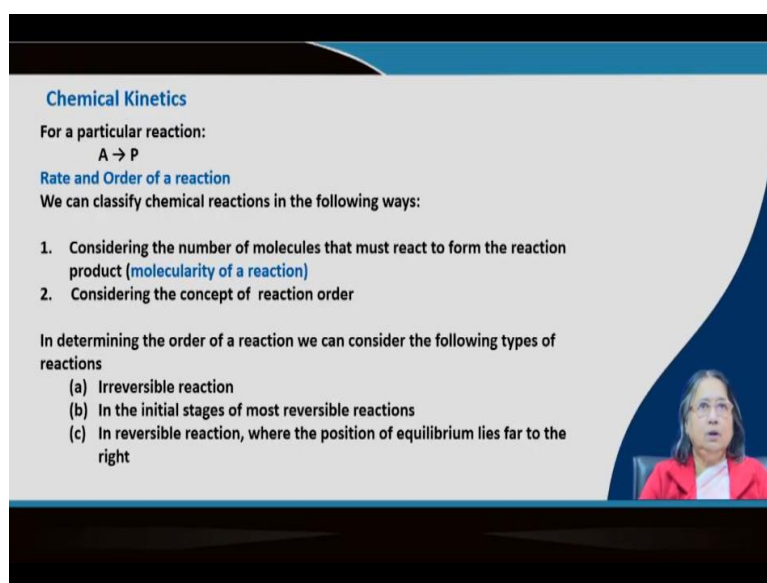
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Dr. Khushi

This slide features a blue header with the title 'Chemical Kinetics' in yellow. Below the header, a list of four topics is presented with right-pointing chevrons. At the bottom left, the NPTEL logo is visible. At the bottom right, there is a small inset video of a woman with dark hair wearing a red jacket.

This is my twelfth lecture and in this lecture under chemical kinetics, I will cover the rate of a reaction, the order of a reaction, molecularity of a reaction, and determination of order by using differential rate law.

(Refer Slide Time: 02:20)



Chemical Kinetics

For a particular reaction:
 $A \rightarrow P$

Rate and Order of a reaction

We can classify chemical reactions in the following ways:

1. Considering the number of molecules that must react to form the reaction product (**molecularity of a reaction**)
2. Considering the concept of reaction order

In determining the order of a reaction we can consider the following types of reactions

- (a) Irreversible reaction
- (b) In the initial stages of most reversible reactions
- (c) In reversible reaction, where the position of equilibrium lies far to the right

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Dr. Khushi

This slide has a blue header with the title 'Chemical Kinetics'. It starts with the text 'For a particular reaction:' followed by the chemical equation $A \rightarrow P$. Below this, the section 'Rate and Order of a reaction' is highlighted in blue. The text 'We can classify chemical reactions in the following ways:' is followed by a numbered list of two points. The first point is further detailed with a sub-list of three types of reactions. At the bottom left, the NPTEL logo is present. At the bottom right, there is a small inset video of the same woman in the red jacket.

So, to talk about the chemical kinetics let us start with a very simple example. Say for example, A is a single reactant which is giving to a single product P. Now, rate and order of a reaction is very important. We can classify the chemical reaction in two different ways:

- i) The first is the molecularity of reaction. Molecularity means the number of molecules that must react to form the reaction product.
- ii) The second classification is done in terms of the reaction order.

So, in case of molecularity of reaction, we can tell from the balanced equation. So, in terms of molecularity, there may be unimolecular reaction, there may be bimolecular reaction, there may be termolecular reaction. But in terms of reaction order, this order has to be determined by experiment. We cannot just directly from seeing a balanced reaction. Sometimes, order of the reaction is 2 or 1 or 0. Sometimes, the molecularity and order may be the same. But not necessarily it will be the same. It may be different also. That is a very important concept for chemical kinetics. Now, for which type of reactions we should determine the order? There are 3 types of reactions. Among them the first one is the irreversible reaction. I already discussed about irreversible and reversible reaction, in the chemical equilibrium chapter. Next, we can determine order in the initial stages of most reversible reactions. Now we can also determine order of reaction for reversible reaction, where the position of equilibrium lies far to the right. This concept I have already given when I was discussing the equilibrium. So, far to the right means, it is almost going to the completion. In that case also, we can determine the order of the reaction.

(Refer Slide Time: 05:57)

Chemical Kinetics

Differential rate law

For a particular reaction:
 $A \rightarrow P$

Rate of disappearance of $A = -dC_A / dt = k (C_A)^n$
 (Rate equation or Rate expression)

Where k is the proportionality constant and it is called 'rate constant', and n is the 'order of the reaction'.

Taking log both sides we get
 $\log (-dC_A / dt) = \log k + n \log C_A$

Or we can write
 $\log (-d[A] / dt) = \log k + n \log [A]$

So experimental results may be plotted to find out the 'reaction order' and 'rate' as shown in the graph.

'Order of a reaction' is experimentally determined.

So fractional reaction orders (e.g. 1.5 or 0.5) is also possible.

However, for the solution of many rate problems an integer value of the reaction order is assumed.

The graph shows $\log(-d[A]/dt)$ on the y-axis and $\log[A]$ on the x-axis. Three lines are plotted: a horizontal line for 'Zero order', a line with a slope of 1 for 'First order', and a line with a slope of 2 for 'Second order'.

Now, what is the order of the reaction, that we must know. We have already got some idea about the rate. Say for the following example ((1)):



So, we can consider rate of disappearance of A as the rate of the reaction. That means, we are considering the reactant A. As it is the reactant, so minus sign should be applied. So, $-dC_A/dt$ is the rate. And so rate is related to the concentration in some way. How it is? It can be stated in the following way:

$$\text{Rate of disappearance of } A = -dC_A/dt = k(C_A)^n \dots \dots \dots (2)$$

Concentration of A can be expressed in two ways: [A] and (C_A).

So, in (2), C_A is the concentration of A at a particular time at time t, n is the order of the reaction, and k is a constant which is called the specific rate constant or it also called rate constant. So, this is something similar to that the equilibrium constant. We have already learnt that equilibrium constant does not depend on the concentration. Similarly rate constant also does not depend on the concentration. It depends on the temperature, but it does not depend on the concentration. And depending on the order of the reaction, the unit will change. The unit of k will change, but the unit of rate is the same. So, if you express the concentration in terms of moles per litre, and time in second; then, unit of k will be moles per litre per second. Or if you express the time in terms of hour, then it will be moles per litre per hour. If you express the concentration in terms of milligram per litre, then it will be milligram per litre per second or per hour.

So, unit of rate will be the same, irrespective of the first order or zero order or second order reactions. Now, if you take logarithm of both sides of rate expression (2):

$$\log(-dC_A/dt) = \log k + n \log C_A \dots \dots \dots (3)$$

or

$$\log(-d[A]/dt) = \log k + n \log [A] \dots \dots \dots (4)$$

$\log dC_A / dt = \log k + n \log C_A$; $\log k + n \log C_A$. Or you can write that, in this way you can express or otherwise this concentration term you can write in this way also.

Minus sign is placed before d[A]/dt because it is the reactant. Now, if by experiment you can determine the value of log(-d[A]/dt) and then at different concentrations of A, if you plot log[A] in the x axis and in the y axis, then, depending on the order of the reaction, you will get the curves as shown in the previous slide. All the curves represent straight line, but the slope will be different. In case of a second order reaction, you will get slope 2. In case of first order reaction, you will get the slope 1. And in case of zero order reaction, you will get a straight line which is the, which is parallel to the x axis. You also need to know that; you are obtaining order of the reaction from the experiment, so it may be either integer or it may be fraction also. Say for example, it can be 1.5, 0.5 etc. So, order can be a fraction also. Say for example, acetaldehyde decomposition at 450 K. At high temperature, you will see that the order is 1.5. But sometimes, in practical purpose; say for example, you see, the slope is like 0.95, then you can think that, it is close to 1. So, you can tell that, order is 1. So, it is first order reaction.

(Refer Slide Time: 12:04)

Chemical Kinetics

Swinbourne (1971):
Order with respect to time
 For a particular reaction:
 $A \rightarrow P$

It is understandable that, the instantaneous rate $(-dC_A / dt)$ of change of reactant concentration at a specific time is difficult to determine.


How to overcome this problem?
 This problem was overcome by Swinbourne (1971) in the following way:

- It was assumed that, at the midpoint of the time interval, Δt , $dC / dt = \Delta C / \Delta t$.
- Say for example \bar{C} is the midpoint for the concentration interval, ΔC , then we can write

$$\log(-\Delta C_A / \Delta t) = \log k + n \log \bar{C}_A$$

Now if the reactant concentrations are measured experimentally at certain time intervals, then a reaction order can be determined from the slope of the straight line obtained by plotting $\log(-\Delta C_A / \Delta t)$ vs. $\log \bar{C}_A$.

↳ This has been designated as 'order with respect to time'.



Now, it is understandable that from the concept of instantaneous rate, $(-dC_A/dt)$, that it is the slope at a particular point. As the time difference is very, very small, so, to determine the instantaneous rate, is difficult. So, how then you will get the order of the reaction by using the previous expression? To overcome this difficulty, Swinbourne in 1971, developed two different methods. One is the order with respect to time and the other is order with respect to concentration. By these methods the order of the reaction can be determined easily. He assumed that at the midpoint of the time interval Δt , $dC_A/dt = \Delta C_A/\Delta t$ and C_{avg} is the midpoint of the interval ΔC_A . Applying this to (3),

$$\log(-\Delta C_A/\Delta t) = \log k + n \log C_{avg} \dots \dots \dots (3)$$

I will show some examples, then, it will be clearer.

(Refer Slide Time: 15:18)


Chemical Kinetics

Swinbourne (1971):
Order with respect to time
 The following experimental data are obtained from a batch reactor:

Plot of $\log(-\Delta C_A / \Delta t)$ vs. $\log \bar{C}_A$???

Time (min)		Reactant conc. C_A (mg/L)	
20	132		
32	68		
41	42		
50	26		

t	C_A	ΔC_A	Δt	$(-dC_A/dt)$	\bar{C}_A	$\log(-dC_A/dt)$	$\log \bar{C}_A$
20	132	-64	12	5.4	100	0.73	2.00
32	68	-26	9	2.9	55.0	0.46	1.74
41	42	-16	9	1.8	34.0	0.25	1.53



An example from a batch reactor has been presented and concentration of reactants at four-time intervals 20, 32, 41 and 50 min has been given. A table has to be prepared from the given data (as shown below):

Time (min)	Reactant concentration C_A (mg/L)	
20	132	
32	68	
41	42	
50	26	

t	C_A	ΔC_A	Δt	$-\left(\frac{\Delta C_A}{\Delta t}\right)$	\bar{C}_A	$\log\left(-\frac{\Delta C_A}{\Delta t}\right)$	$\log \bar{C}_A$
20	132	-64	12	5.4	100	0.73	2.00
32	68	-26	9	2.9	55.0	0.46	1.74
41	42	-16	9	1.8	34.0	0.25	1.53
50	26						

The first column of the table represents different time intervals at which concentration of the reactant was measured, second column represents corresponding concentration of the reactant. The third column indicates difference in concentration ($-\Delta C_A$) and the fourth one records difference in time interval (Δt). The fifth column shows the $-\Delta C_A/\Delta t$ value and sixth column shows C_{avg} values. By taking logarithm of fifth and sixth column and plotting them you can get the order of the reaction.

(Refer Slide Time: 18:05)

20:18 / 23:22


Chemical Kinetics

Swinbourne (1971):
Order with respect to concentration

In this method the following steps are followed:

- The experiment is carried out with several (minimum 4 runs) initial concentrations of the reactant (say A). These concentrations are considered as concentrations at zero time.
- Then once the reaction starts, after say one min, the concentrations of A are again determined for each run.
- Then $\log(-\Delta C_A / \Delta t)_0$ and $\log(C_A)_0$ are calculated.
- Finally $\log(-\Delta C_A / \Delta t)_0$ is plotted vs. $\log(C_A)_0$
- The order of the reaction is given by the slope of the linear plot.

A reaction order determined by this method is termed as 'order with respect to concentration'.



Now, let us see another method explained by Swinbourne, 1971. This method determines the order of the reaction with respect to concentration. In this method, the experiment is carried out with several minimum four runs with different initial concentration. After the reaction starts after just small interval say 1 minute, four different concentrations are again measured. Now $\log(-\Delta C_A / \Delta t)_0$ and $\log(C_A)_0$ at beginning of the reaction are measured for each run and plot of $\log(-\Delta C_A / \Delta t)_0$ vs $\log(C_A)_0$ will give the order of the reaction. It is explained by means of a numerical example as shown below.

(Refer Slide Time: 20:29)

Chemical Kinetics


Swinbourne (1971):
Order with respect to concentration

The following experimental data are obtained from a batch reactor:

Plot of $\log(-\Delta C_A / \Delta t)_0$ vs. $\log(C_A)_0$???

Time (min)	C_A (Run 1) (mg/l)	C_A (Run 2) (mg/l)	C_A (Run 3) (mg/l)	C_A (Run 4) (mg/l)
0	141.0	235.6	332.8	428.4
1	135.6	226.8	322.2	420.6

Run	$-\frac{dC_A}{dt}_0$	$\log(-\frac{dC_A}{dt}_0)$	$\log(C_A)_0$
1	5.4	0.73	2.15
2	8.8	0.94	2.37
3	12.6	1.10	2.52
4	17.8	1.25	2.63



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Time (min)	C_A (Run 1) (mg/L)	C_A (Run 2) (mg/L)	C_A (Run 3) (mg/L)	C_A (Run 4) (mg/L)
0	141.0	235.6	332.8	488.4
1	135.6	226.8	320.2	470.6

Run	$-\left(\frac{\Delta C_A}{\Delta t}\right)_0$	$\log\left(-\frac{\Delta C_A}{\Delta t}\right)_0$	$\log(C_A)_0$
1	5.4	0.73	2.15
2	8.8	0.94	2.37
3	12.6	1.10	2.52
4	17.8	1.25	2.68

Like the previous numerical example, in this one also a table has been constructed. The first column record number of runs, second one indicates $(-\Delta C_A/\Delta t)_0$, third one indicates $\log(-\Delta C_A/\Delta t)_0$ value, fourth one indicates $\log(C_A)_0$ values. The plot of $\log(-\Delta C_A/\Delta t)_0$ vs $\log(C_A)_0$ will give the order of the reaction.

(Refer Slide Time: 22:50)

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)

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Now this, the, in this lecture what have been covered, you can read from the same two books that I mentioned in my previous lecture (i.e., under Chemical Kinetics), and the same two books you can read to get more elaborative way you can get the concept. Thank you very much for your kind patience.