



INTERNATIONAL COLLEGE
OF PHARMACEUTICAL
INNOVATION

国际创新药学院

Class	Pharm, BioPharm
Course	Fundamentals of Medicinal & Pharmaceutical Chemistry
Code	FUNCHEM.9
Title	Rate laws & orders of reactions
Lecturer	Prof. Xincheng Teng
Date	2024-11-22

Recommended Reading

- General Chemistry - The Essential Concepts
by Chang and Goldsby (7th edition)
Chapter 14: Chemical Kinetics
14.1 The rate of reaction 470
14.2 The rate laws 474
14.3 Relation between reactants conc and time 478

Lecture Outcomes

- Using specific examples, identify a differential rate equation and the corresponding integrated rate equation, explaining the relationship between reactant concentration and reaction rate in terms of a zero, first and second order process.
- Demonstrate how the rate constant 'k' can be obtained graphically from a knowledge of the integrated rate equation.
- Define 'half-life' for a zero and first order process and recall that the half-life for a first order process is constant.
- Apply the 'graphical method', 'initial rates method' or 'half-life method' to work out the order of a reaction.
- The rate law of elementary steps.
- Determine the overall reaction rate from the elementary steps.

Remember that

- “The order of reaction” describes the degree of dependence of the reaction rate on the concentrations of reactants, which is determined only by experiment.
- The overall reaction order is The sum of the powers to which all reactant concentrations are raised in the rate law.
- Reaction order could be:
 1. Zero order: $\text{Rate} = k$ (where reactant concentration has no effect on the rate).
 2. First order: $\text{Rate} = k[\text{reactant}]^1$ (where doubling reactant concentration doubles the reaction rate)
 3. Second order: $\text{Rate} = k[\text{reactant}]^2$ (where doubling reactant concentration quadruples the reaction rate)
 4. Pseudo First order: when?

How to define reaction order

- **Reaction order** is determined only experimentally.
- **Stoichiometric coefficient** of the reactant in the overall balanced equation (the number of moles reacting) might be different from the reaction order with regard to this particular reactant.
- So.. How can we define the reaction order?
 1. **Initial rates method (differential rate law)**
 2. **Graphical method (Integrated rate law)**
 3. **Half-life method**

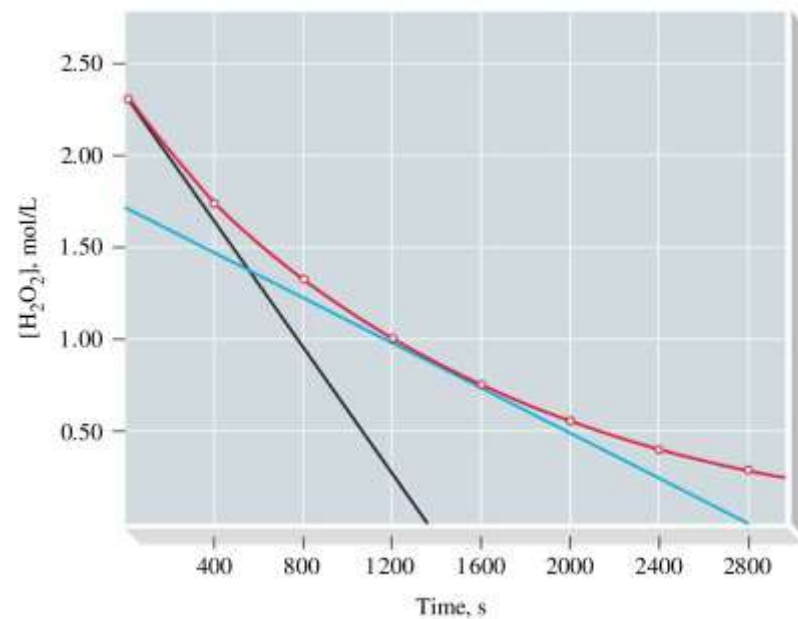
Method 1. Initial Rates Method (Differential rate laws)

In this method the rate measurements are made close to the beginning of reaction because we know the initial reactants' concentrations.

The initial rate of reaction is determined from the gradient of the tangent at the start of the reaction.

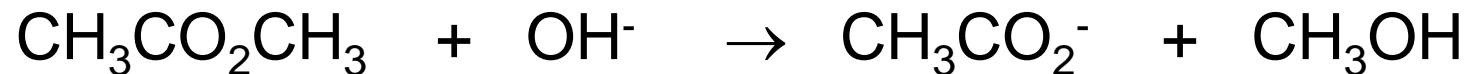
The experiment is repeated several times using different initial concentrations (to get the initial rate at various concentrations of reactant).

From the degree of dependence of reaction rate on reactant(s) concentration, the reaction order for every reactant is identified and overall differential rate law is deduced.



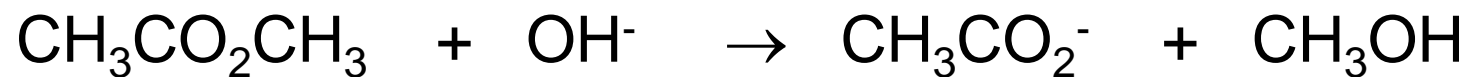
Example:

Find the rate equation for the following reaction



- To do this you need to identify the order of reaction for each reactant.
- This is found by using the initial rates data in the given table below:

Experiment	Initial Concentrations		Initial Reaction Rate
	[CH ₃ CO ₂ CH ₃]	[OH ⁻]	Mol/L s at 25 ^o C
1	0.05 M	0.05 M	0.00034
2	0.05 M	0.10 M	0.00069
3	0.10 M	0.10 M	0.00137



Experiment	Initial Concentrations		Initial Reaction Rate
	[CH ₃ CO ₂ CH ₃]	[OH ⁻]	Mol/L s at 25 ⁰ C
1	0.05 M	0.05 M	0.00034
2	0.05 M	0.10 M	0.00069
3	0.10 M	0.10 M	0.00137

From the table we find that:

By comparing Experiments 1 & 2

[CH₃CO₂CH₃] is kept constant and it is 1st order for [OH⁻]

By comparing experiments 2 & 3

[OH⁻] is kept constant and it is 1st order for [CH₃CO₂CH₃]

So, Rate law is: **Rate = $k[\text{CH}_3\text{CO}_2\text{CH}_3][\text{OH}^-]$**

Overall reaction order is **second order** ($1 + 1 = 2$)

How to find k (rate constant) in this example?

For experiment 1:

Reaction Rate = $0.00034 \text{ mol/Ls} = 3.4 \times 10^{-4} \text{ mol/Ls}$

Concentration of both reactants was 0.05 mol/L

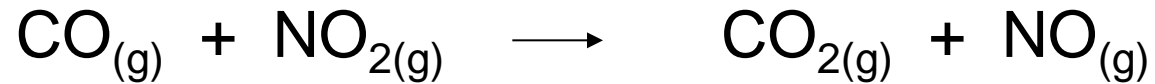
Rate = **k** (0.05 mol/L) (0.05 mol/L)

$3.4 \times 10^{-4} \text{ mol/Ls} = \textbf{k}$ (0.05 mol/L) (0.05 mol/L)

$$k = \frac{3.4 \cdot 10^{-4} \text{ mol/L s}}{(0.05 \text{ mol/L})(0.05 \text{ mol/L})} = \textbf{0.136 L/mol s}$$

Try this one yourself:

The following is the data for the reaction between CO and NO₂ at a temp of 510 K.



Find the rate equation and the value of the rate constant

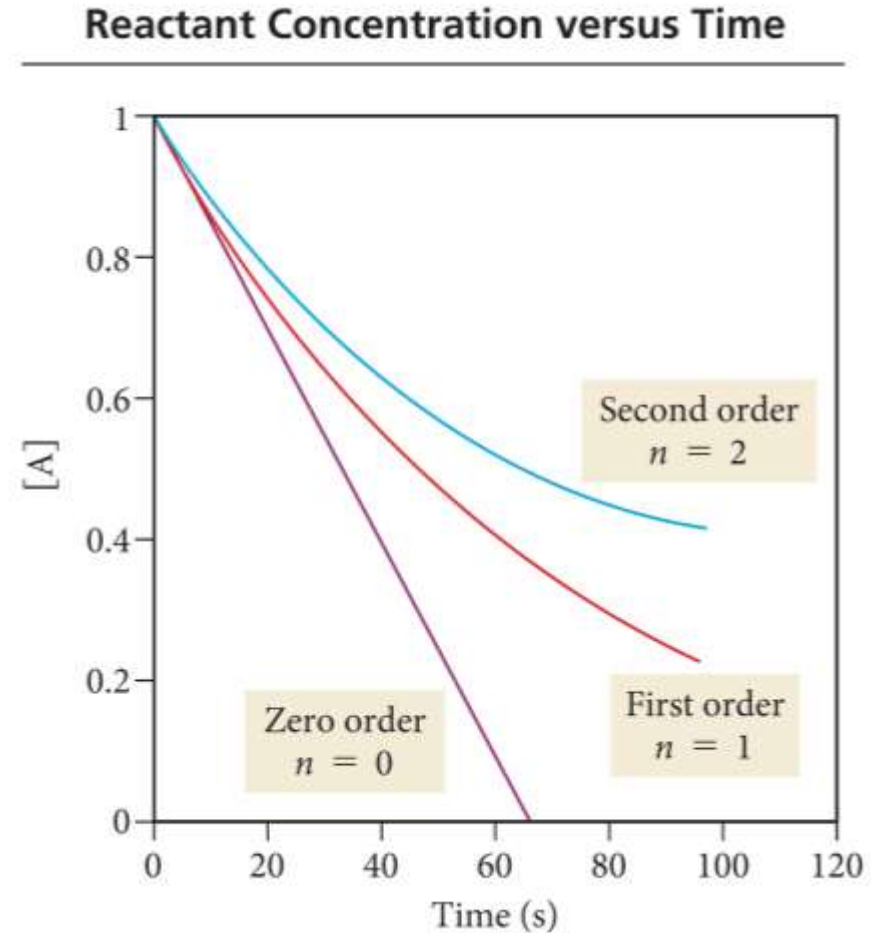
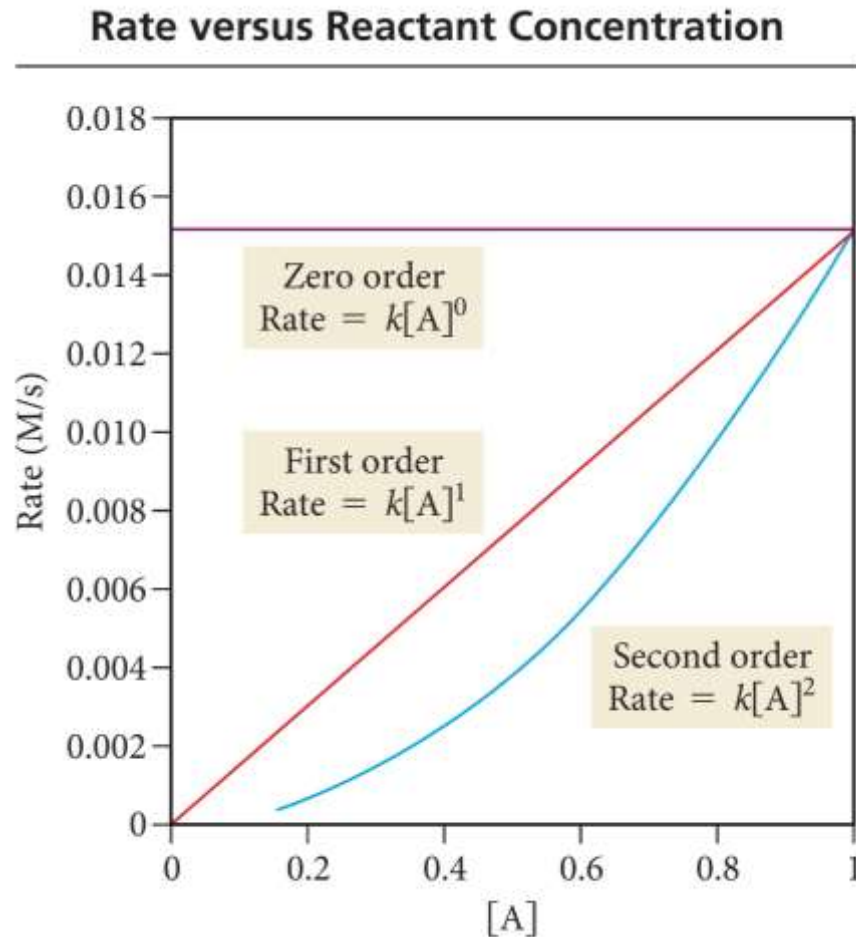
	Initial concentrations		
Experiment	[CO] mol/l	[NO ₂] mol/l	Initial Rate (mol/l h)
1	5.10 x 10 ⁻⁴	0.35 x 10 ⁻⁴	3.4 x 10 ⁻⁸
2	5.10 x 10 ⁻⁴	0.70 x 10 ⁻⁴	6.8 x 10 ⁻⁸
3	5.10 x 10 ⁻⁴	0.175 x 10 ⁻⁴	1.7 x 10 ⁻⁸
4	1.02 x 10 ⁻³	0.35 x 10 ⁻⁴	6.8 x 10 ⁻⁸
5	1.53 x 10 ⁻³	0.35 x 10 ⁻⁴	10.2 x 10 ⁻⁸

Method 2. Graphical Method (Integrated rate laws)

- Integrated rate laws are used to calculate reactant concentration **at any given time.**
- These laws set up a relation between reactant(s) **CONCENTRATION** and **TIME.**
- Using integrated laws, it would be possible to find out the time required for a given amount of reactant to react completely.
- This allows us to calculate the **shelf-life** of medicines, the **half-life** of drugs inside the body and the time-intervals required between **drug doses.**

The Integrated Rate Law

- The **integrated rate law** for a chemical reaction is a relationship between the concentrations of the reactants and time.



Zero-order Integrated Rate Law

- For $A \rightarrow \text{products}$, if it is zero order,

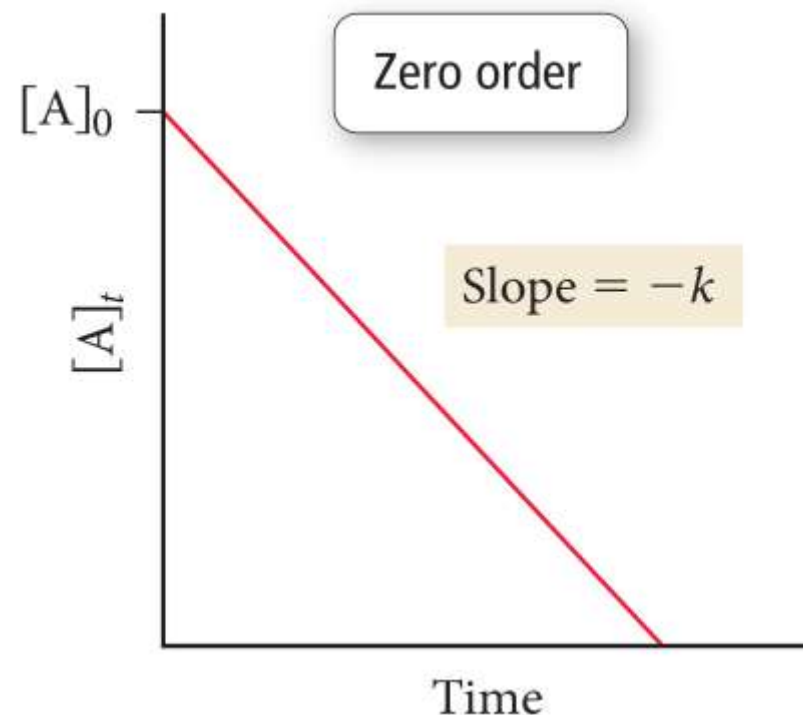
$$\text{Rate} = k[A]^0 = k$$

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t}$$

so, $\frac{-\Delta[A]}{\Delta t} = k$ (differential rate law)

- We can integrate this differential rate law to obtain the **zero-order integrated rate law**

$$[A]_t = -kt + [A]_0$$



Zero-order Integrated Rate Law

Ammonia gas decomposition on a hot tungsten wire is an example for **zero order reaction**



$$\frac{-d[\text{NH}_3]}{dt} = k$$

The integrated rate law for this reaction is:

The diagram illustrates the analogy between the integrated rate law and a linear equation. At the top, a red box contains the equation $[\text{NH}_3] = -kt + [\text{NH}_3]_0$. Below it, another red box contains the general linear equation $y = mx + c$. Four arrows point from the bottom box to the top box: one from 'y' to $[\text{NH}_3]$, one from 'm' to $-k$, one from 'x' to t , and one from 'c' to $[\text{NH}_3]_0$.

$$[\text{NH}_3] = -kt + [\text{NH}_3]_0$$
$$y = mx + c$$

First-order Integrated Rate Law

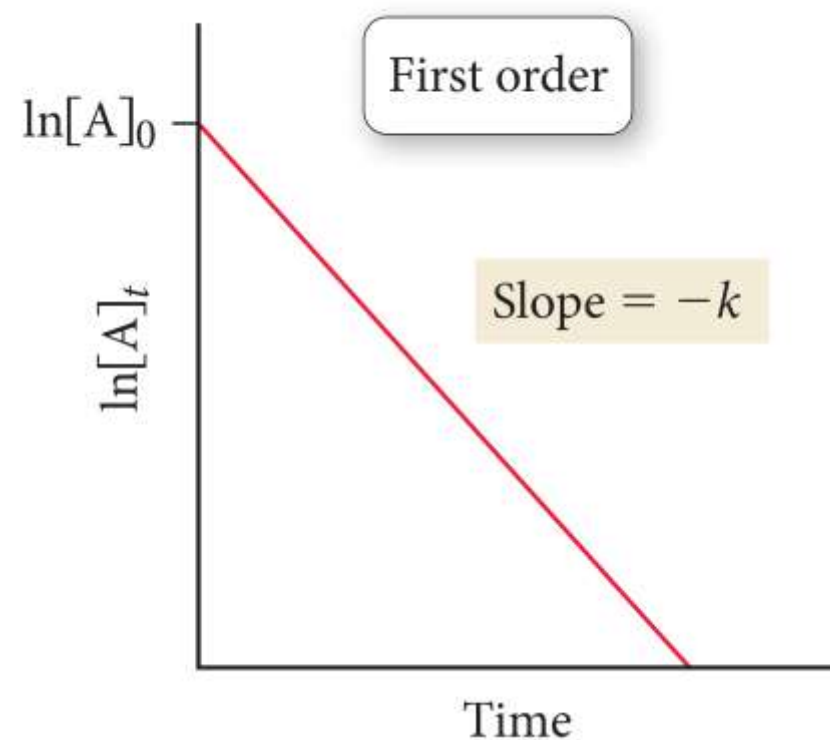
- For $A \rightarrow$ products, if it is first order,

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]$$

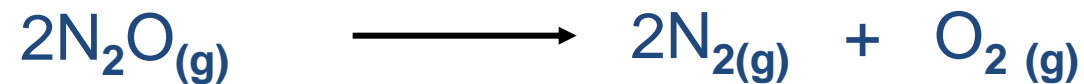
- After integration,

$$\ln[A]_t = -kt + \ln[A]_0$$

- For a first-order reaction, a plot of the natural log of the reactant concentration as a function of time yields a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$.



First-order Integrated Rate Law



$$\text{Rate} = k [\text{N}_2\text{O}] \quad \frac{d[\text{N}_2\text{O}]}{dt} = k [\text{N}_2\text{O}]$$

Integrated Rate Law for this reaction is: $\ln [\text{N}_2\text{O}]_t = -kt + \ln [\text{N}_2\text{O}]_0$

$[\text{N}_2\text{O}]_t$ is the concentration at time (t), k is the rate constant and $[\text{N}_2\text{O}]_0$ is the initial concentration of N_2O at time zero.

This equation is also similar to straight line equation

$$\ln [\text{NH}_3] = -kt + \ln[\text{NH}_3]_0$$

$$y = mx + c$$

Second-order Integrated Rate Law

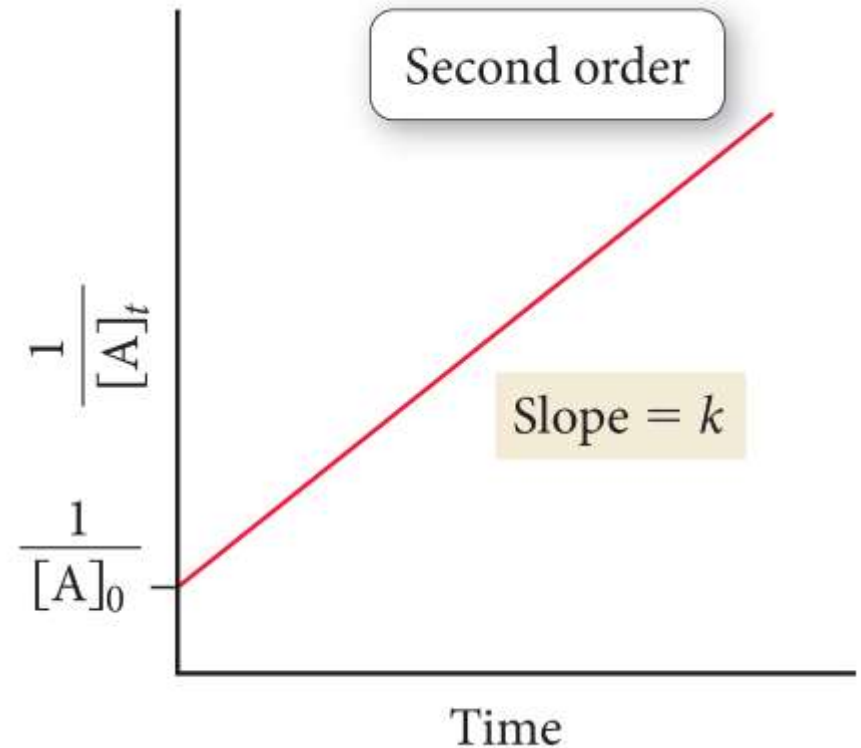
- For $A \rightarrow \text{products}$, if it is second order,

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^2$$

- After integration,

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

- For a second-order reaction, a plot of the inverse of the concentration of the reactant as a function of time yields a straight line with a slope of k and an intercept of $1/[A]_0$.



Second-order Integrated Rate Law



$$\frac{d [\text{CH}_3\text{CHO}]}{dt} = k [\text{CH}_3\text{CHO}]^2$$

Integrated Rate Law for this reaction is:

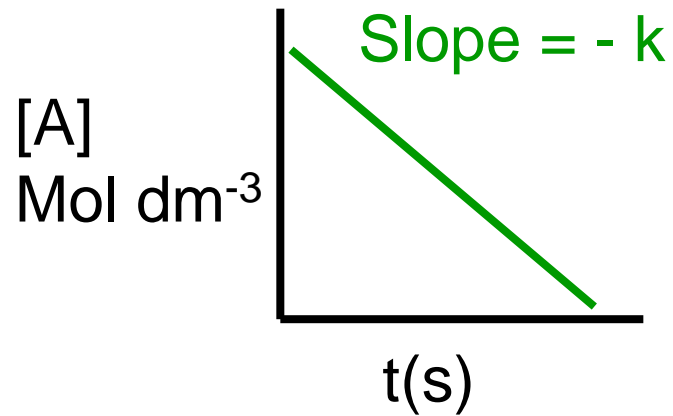
$$\frac{1}{[\text{CH}_3\text{CHO}]_t} = k t + \frac{1}{[\text{CH}_3\text{CHO}]_0}$$

$y = mx + c$

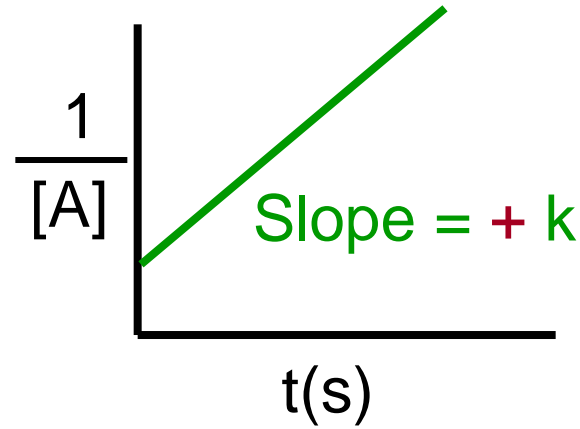
$[\text{CH}_3\text{CHO}]_t$ is the concentration at time (t), k is the rate constant and $[\text{CH}_3\text{CHO}]_0$ is the initial concentration of CH_3CHO at time zero.

This equation too is similar to **straight line** equation.

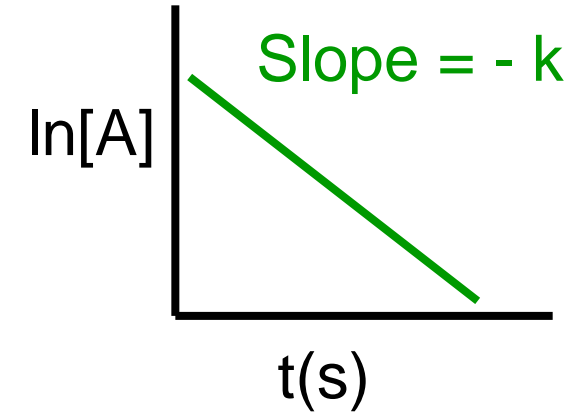
How can you define the reaction order using the graphical method



Zero Order



Second Order



First Order

Order	0	1	2
Plot $[A]$ vs t	Straight line	Curve	Curve
Plot $\ln[A]$ vs t	Curve	Straight line	Curve
Plot $1/[A]$ vs t	Curve	Curve	Straight line

Method 3. Half Life Method

- The half-life of a reaction ($t_{1/2}$): is the time required for the concentration of a reactant to decrease to half of its initial concentration.
- The longer the half life the slower will be the reaction.
- Half life ($t_{1/2}$) could be either dependent or independent of concentration (based on integrated rate law).
- In zero order and second order reactions, the ($t_{1/2}$) is dependent on concentration, while;
- In first order reactions, the ($t_{1/2}$) is independent of concentration, and is therefore constant throughout the reaction.

Half Life Of Zero Order Reaction

- For the zero-order reaction,

$$[A]_t = -kt + [A]_0$$

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

- For the zero-order reaction, the half-life depends on the initial concentration.
- The half-life gets shorter as the concentration decreases.

Half Life Of First Order Reaction

- For the first-order reaction,

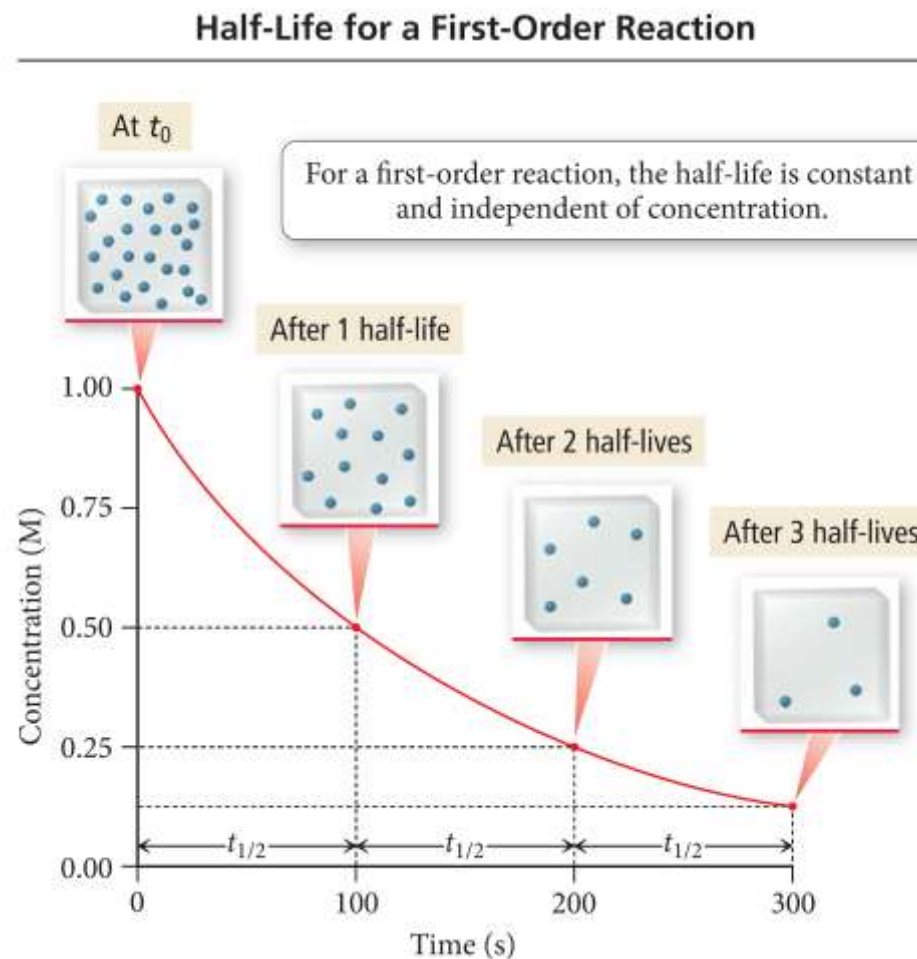
$$\ln[A]_t = -kt + \ln[A]_0$$

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

$$\ln \frac{1}{2} \frac{[A]_0}{[A]_0} = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- For the first-order reaction, $t_{1/2}$ is independent of the initial concentration .



Half Life Of Second Order Reaction

- For the second-order reaction,

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

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

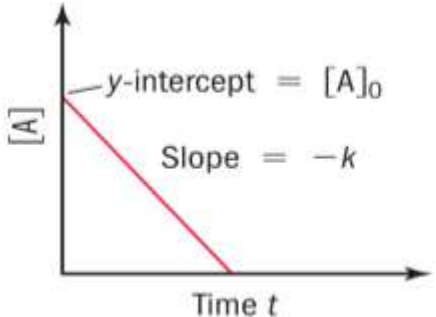
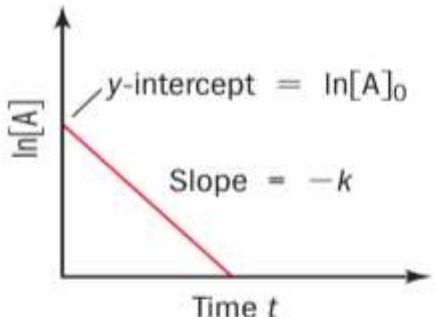
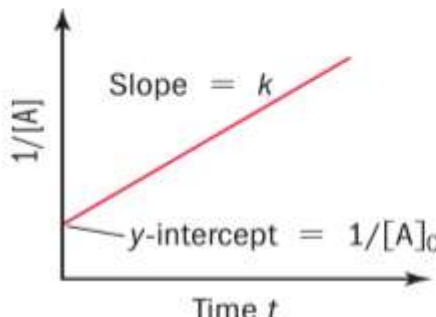
$$t_{1/2} = \frac{1}{k[A]_0}$$

- For the second-order reaction, the half-life depends on the initial concentration. The half-life gets longer as the concentration decreases.

How can you define the reaction order using the half life method

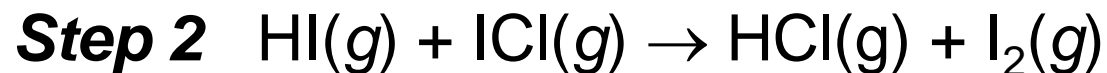
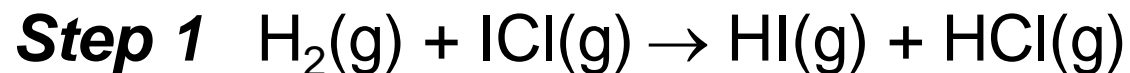
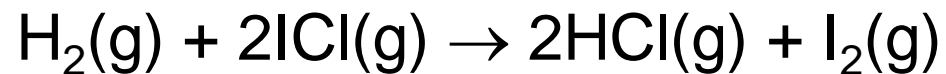
- This method is usually used to check whether the reaction is **first order** or not.
- Since the $(t_{1/2})$ in first order reaction is independent of concentration, repeated cycles of 50% reduction of concentration are taking place every half life.
- This is a unique feature for **first order** reactions

Summary

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$	 <p>y-intercept = $[A]_0$ Slope = $-k$</p>	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$	 <p>y-intercept = $\ln[A]_0$ Slope = $-k$</p>	$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	 <p>Slope = k y-intercept = $1/[A]_0$</p>	$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

Reaction Mechanisms

- The **reaction mechanism** is the series of individual chemical steps by which an overall chemical reaction occurs.



- Each step in a reaction mechanism is an **elementary step**, which cannot be broken down into simpler steps (they represent the exact species that are colliding in the reaction).
- A **reaction intermediate** (e.g. HI in the above example) forms in one elementary step and is consumed in another.

Rate Laws For Elementary Steps

- An elementary step occurs through the collision of the reactant particles, thus the rate is proportional to the product of the concentrations of those particles.

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \longrightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \longrightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

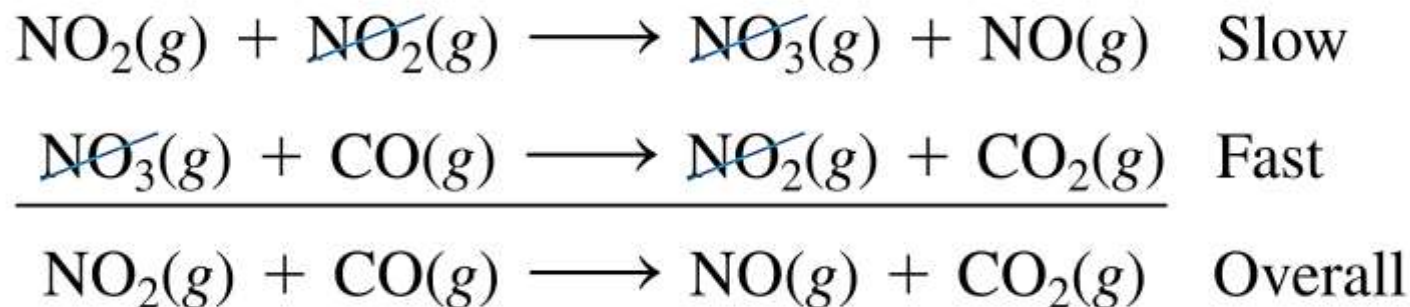
Rate-determining Step

- In most chemical reactions, one of the elementary steps — called the **rate-determining step** — is much slower than the others.
- The rate-determining step in a reaction mechanism limits the overall rate of the reaction and therefore determines *the rate law for the overall reaction*.



Overall Reaction Rate Laws

- The elementary steps in the mechanism must sum to the overall reaction.
- The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.



- Overall reaction rate = $k[\text{NO}_2]^2$

Example 1

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when $[\text{NO}] = 12.0 \times 10^{-3} \text{ M}$ and $[\text{H}_2] = 6.0 \times 10^{-3} \text{ M}$.

Experiment	$[\text{NO}] \text{ (M)}$	$[\text{H}_2] \text{ (M)}$	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Strategy We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant. We assume that the rate law takes the form

$$\text{rate} = k[\text{NO}]^x[\text{H}_2]^y$$

Experiment	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Look at experiments 1 and 2: [H₂] is constant
 As you double [NO], the rate quadruples

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \text{ M/s}}{1.3 \times 10^{-5} \text{ M/s}} \approx 4$$

We say then that the order of reaction with respect to [NO] is 2

Experiment	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Look at experiments 2 and 3: [NO] is constant
 As you double [H₂], the rate doubles

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5} \text{ M/s}}{5.0 \times 10^{-5} \text{ M/s}} = 2$$

We say then that the order of reaction with respect to [H₂] is 1

$$\text{Rate} = k [\text{H}_2]^1 [\text{NO}]^2$$

Experiment	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Now asked to work out the rate constant:

$$\text{Rate} = k [\text{H}_2]^1 [\text{NO}]^2$$

$$k = \frac{\text{Rate}}{[\text{H}_2]^1 [\text{NO}]^2}$$

$$\frac{5.0 \times 10^{-5} \text{ M/s}}{(2.0 \times 10^{-3} \text{ M})^1 (10.0 \times 10^{-3} \text{ M})^2} = 2.5 \times 10^2 \text{ /M}^2 \text{ s}$$

Experiment	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Now asked to work out rate when
[NO] = 12.0×10^{-3} M and [H₂] = 6.0×10^{-3} M:

$$\text{Rate} = k [\text{H}_2]^1 [\text{NO}]^2 \qquad k = 2.5 \times 10^2 \text{ /M}^2.\text{s}$$

$$\text{Rate} = (2.5 \times 10^2 \text{ /M}^2.\text{s}) (6.0 \times 10^{-3} \text{ M})^1 (12.0 \times 10^{-3} \text{ M})^2$$

$$\text{Rate} = 2.2 \times 10^{-4} \text{ M/s}$$

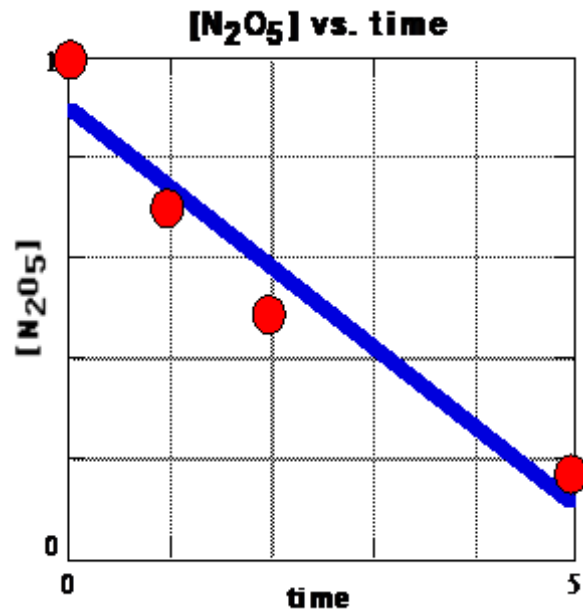
Example 2

Using integrated rate laws and the data shown in the Table below, identify whether this reaction is a zero order or first order.

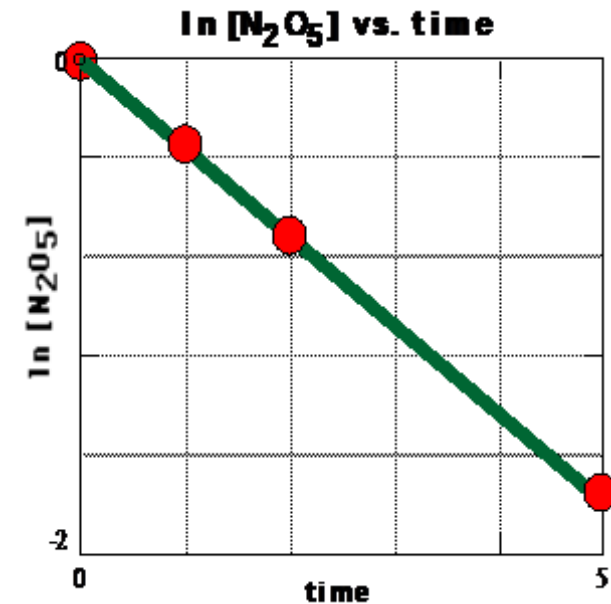


Time (min)	[N ₂ O ₅] M	Ln[N ₂ O ₅]
0	1.00	0
1.0	0.705	- 0.35
2.0	0.497	- 0.70
5.0	0.173	- 1.75

1. First: plot $[\text{N}_2\text{O}_5]$ vs time and see if you get a straight line with negative slope. If not, it is not a zero order reaction.
2. Second: plot $\ln [\text{N}_2\text{O}_5]$ vs time and if you got a straight line with negative slope it is a first order reaction.



Plot of conc. vs. time does not fit straight line.

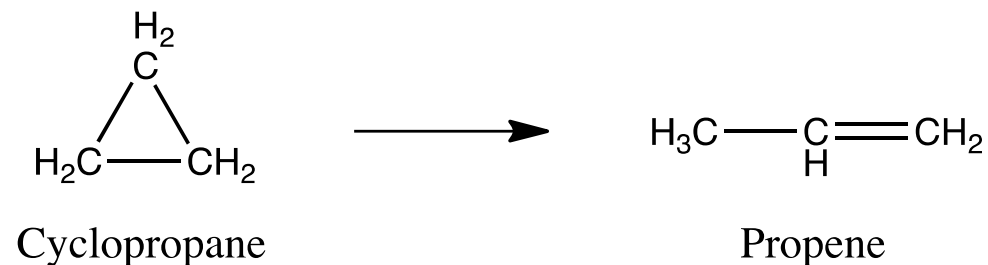


Plot of " $\ln [\text{N}_2\text{O}_5]$ " vs. time is a straight line!

$$\text{Rate} = k [\text{N}_2\text{O}_5]$$

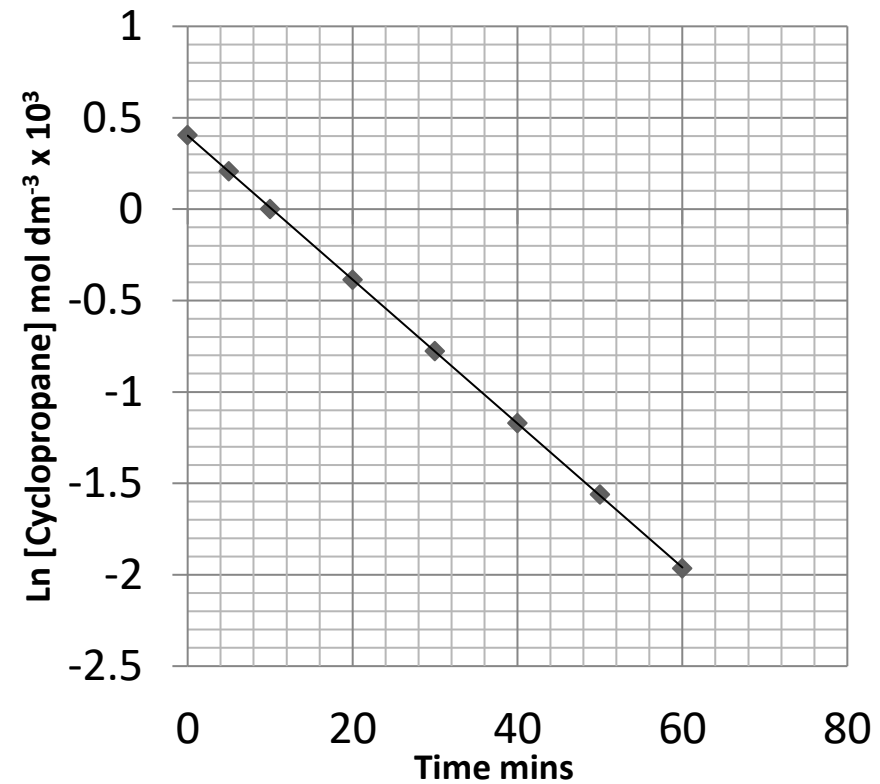
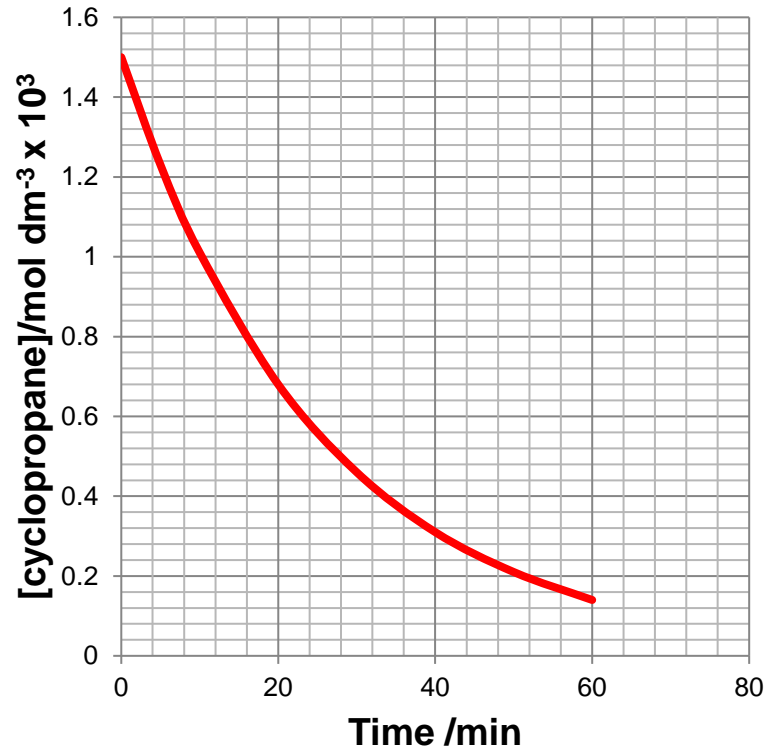
Example 3

When cyclopropane is heated to 750 K it isomerises to propene as showed in the equation below.



Using the data in the table, find out whether this reaction follows zero order or first order kinetics.

T (mins)	[cyclopropane] x 10 ⁻³ mol dm ⁻³	ln [Cyclopropane]
0	1.5	0.405
5	1.23	0.207
10	1.01	0.001
20	0.68	-0.386
30	0.46	-0.777
40	0.31	-1.171
50	0.21	-1.561
60	0.14	-1.966

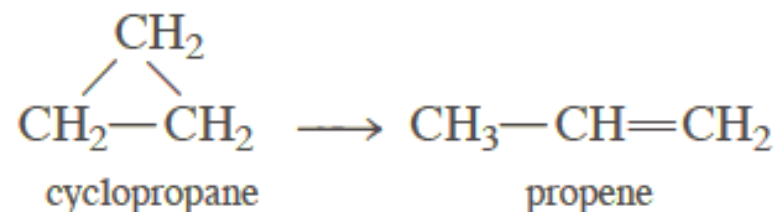


The plot of $\ln[\text{conc}]$ vs time is a straight line showing that the reaction is **first order**

The slope of this line is -0.04 min^{-1} $-k = -0.04 \text{ min}^{-1}$
 $k = 0.04 \text{ min}^{-1}$

Example 4

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C .



(a) If the initial concentration of cyclopropane was 0.25 M , what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M ? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

$$\ln [A]_t = -kt + \ln [A]_0$$

- a) we are given $[A]_0 = 0.25 \text{ M}$ and asked for $[A]_t$ after 8.8 min.
- b) we are asked to calculate the time it takes for cyclopropane to decrease in conc. from 0.25 M to 0.15 M .
- c) No concentration values are given. However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be: $(100\% - 74\% = 26\%)$.

we are given $[A]_0 = 0.25 \text{ M}$ and asked for $[A]_t$ after 8.8 min

a) we note that because k is given in units of s^{-1} , we must first convert 8.8 min to seconds:

$$\begin{aligned} 8.8 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} &= 528 \text{ s} \\ \ln [A]_t &= -kt + \ln [A]_0 \\ &= -(6.7 \times 10^{-4} \text{ s}^{-1})(528 \text{ s}) + \ln (0.25) \\ &= -1.74 \\ [A]_t &= e^{-1.74} = 0.18 \text{ M} \end{aligned}$$

b) Calculate the time it takes for cyclopropane to decrease in conc. to 0.15 M.

$$\begin{aligned} \ln [A]_t &= -kt + \ln [A]_0 \\ \ln \frac{0.15 \text{ M}}{0.25 \text{ M}} &= -(6.7 \times 10^{-4} \text{ s}^{-1})t \\ t &= 7.6 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 13 \text{ min} \end{aligned}$$

Example 4

c) How long will it take (in minutes) to convert 74% of the starting material? (100% - 74% = 26%).

So if $[A]_0 = 0.25 \text{ M}$ then $26\% = (0.25 \times 26)/100 = 0.065 \text{ M}$

$$\ln [A]_t = -kt + \ln [A]_0$$

$$\ln (0.065) = - (6.4 \times 10^{-4} \text{s}^{-1}) t = \ln (0.25)$$

$$t = 2,014.9 \text{ s or approx. 33 mins}$$

Example 5

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4} \text{ s}^{-1}$ at 700°C :



Calculate the half-life of the reaction in minutes.

Strategy:

To calculate the half-life we can use the following equation.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

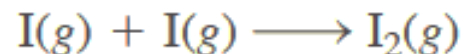
Since the rate constant is provided in “second units” and half-life should be calculated in minutes, we need to convert the product of the equation from seconds to minutes.

Solution:

$$\begin{aligned}t_{\frac{1}{2}} &= \frac{0.693}{k} \\&= \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}} \\&= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\&= 21.5 \text{ min}\end{aligned}$$

Example 6

Iodine atoms combine to form molecular iodine in the gas phase



This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9 / \text{M} \cdot \text{s}$ at 23°C . (a) If the initial concentration of I was 0.086 M , calculate the concentration after 2.0 min . (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M .

Solution:

- a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant to apply them in the following equation:

$$\frac{1}{[\text{A}]_t} = k t + \frac{1}{[\text{A}]_0}$$
$$\frac{1}{[\text{A}]_t} = (7.0 \times 10^9 / \text{M} \cdot \text{s}) \left(2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.086 \text{ M}}$$

$$[\text{A}]_t = 1.2 \times 10^{-12} \text{ M}$$

To calculate half-lives:

b) For $[I]_0 = 0.60 \text{ M}$

$$\begin{aligned}t_{\frac{1}{2}} &= \frac{1}{k[A]_0} \\&= \frac{1}{(7.0 \times 10^9 / \text{M} \cdot \text{s})(0.60 \text{ M})} \\&= 2.4 \times 10^{-10} \text{ s}\end{aligned}$$

For $[I]_0 = 0.42 \text{ M}$

$$\begin{aligned}t_{\frac{1}{2}} &= \frac{1}{(7.0 \times 10^9 / \text{M} \cdot \text{s})(0.42 \text{ M})} \\&= 3.4 \times 10^{-10} \text{ s}\end{aligned}$$

Check These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s).