

## Rate Laws (2)

There are two types of rate law:

- 1) The differentiated rate law or simply rate law, shows how the rate of a reaction depends on concentrations.
- 2) The integrated rate law shows how the concentrations of species in the reaction depend on time. Rate law can be converted into equations that tell us what the concentrations of the reactants or products are at any time during the course of reaction.

## The Differentiated Rate Law

### How can a reaction rate be explained?

Rate law describes the way in which reactant concentration affects reaction rate.

For a reaction that involves a single reactant, the rate law takes the following form.

$$\text{Rate} = k [\text{reactant 1}]^n$$

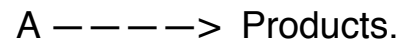
***k*: rate constant**

The exponent  $n$ , is called the order of the reaction. It is usually a whole number, often 1 or 2.

Order in chemistry, is a classification of the chemical reactions that depends on the number of molecules that appear to enter into the reaction.

Reaction orders cannot be determined from a chemical equation. They must be found by experiment.

## Rate law for reactions involving a single reactant



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

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

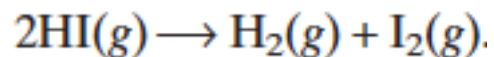
If  $n = 0$  then the reaction is zero order. The rate is constant and does not change with the change of concentration.

If  $n = 1$  then the reaction is first order . Doubling the concentration of A will double the rate of formation of the products.

If  $n = 2$ , then the reaction is second order. When the concentration of A is doubled, the rate of formation of the product will be multiplied by 4.

A reaction is  $n$ th order if doubling the concentration causes a  $2^n$  increase in rate.

Example:



Experiment	[HI] (M)	Rate (M/s)
1	0.015	$1.1 \times 10^{-3}$
2	0.030	$4.4 \times 10^{-3}$
3	0.045	$9.9 \times 10^{-3}$

$$\text{rate} = k[\text{HI}]^n$$

Experiment 2: rate 2 =  $k [\text{HI}]^n_2$

Experiment 1: rate 1 =  $k [\text{HI}]^n_1$

$$\text{rate 2} / \text{rate 1} = k [\text{HI}]^n_2 / k [\text{HI}]^n_1 = ([\text{HI}]_2 / [\text{HI}]_1)^n$$

$$4.4 \times 10^{-3} / 1.1 \times 10^{-3} = (0.03 / 0.015)^n$$

$$4 = (2)^n$$

$$n = 2$$

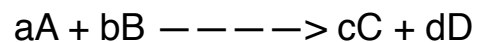
When the concentration changes by a factor of 2, the rate changes by 4 or  $2^2$ . Therefore,  $n = 2$  and the reaction order is 2.

We can determine the rate of the reaction ( $k$ ) using the data of any experiment. For Experiment 1:

$$k = \text{rate 1} / [\text{HI}]^2_1 = 1.1 \times 10^{-3} / (0.015)^2 = 1.1 \times 10^{-3} / 0.225 \times 10^{-3} = 4.88 \text{ (1/M.s)}$$

## Rate laws for reactions with more than one reactant.

For the general reaction:



$$\text{Rate} = k [A]^m [B]^n$$

The overall order of the reaction =  $m + n$

### Calculating m:

Choose conditions where the concentration of B is constant. Compare the concentration of A at different time will lead to knowing the value of m.

### Calculating n:

Choose conditions where the concentration of A is constant. Compare the concentration of B at different time will lead to knowing the value of n.

## Rate laws for several reactants

When a reaction has more than one reactant, a term in the rate law corresponds to each.

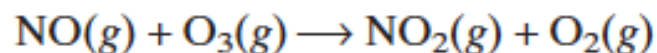


There is an order associated with each term:

$$\text{rate} = k[\text{Br}^-]^{n_1}[\text{H}_2\text{O}_2]^{n_2}[\text{H}_3\text{O}^+]^{n_3}$$

For example,  $n_1$  is the reaction order with respect to  $\text{Br}^-$ .

For the reaction:



$$\text{rate} = k[\text{NO}]^{n_1}[\text{O}_3]^{n_2}$$

It was determined experimentally that  $n_1=n_2=1$ .

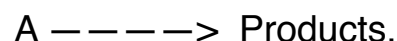
$$\text{rate} = k [\text{NO}][\text{O}_3]$$

This suggests that this reaction has a simple one-step mechanism in which an oxygen atom is transferred when the two reactant molecules collide.

## The Integrated Rate Law Involving a Single Reactant

### Determining the Form of the Rate Law:

Table 12.6 below is a summary of the kinetics for reaction involving a single reactant.



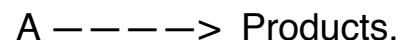
**TABLE 12.6 Summary of the Kinetics for Reactions of the Type  $aA \rightarrow \text{Products}$  That Are Zero, First, or Second Order In  $[A]$**

	Order		
	<i>Zero</i>	<i>First</i>	<i>Second</i>
Rate Law:	Rate = $k$	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus $t$	$\ln[A]$ versus $t$	$\frac{1}{[A]}$ versus $t$
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = $k$
Half-Life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

## Half Life ( $t_{1/2}$ )

Half-life ( $t_{1/2}$ ) is the time required for the concentration of a reactant to decrease to half its original value.

## Zero-Order Rate Laws



For zero-order reaction, the rate is constant. It does not change with concentration;

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

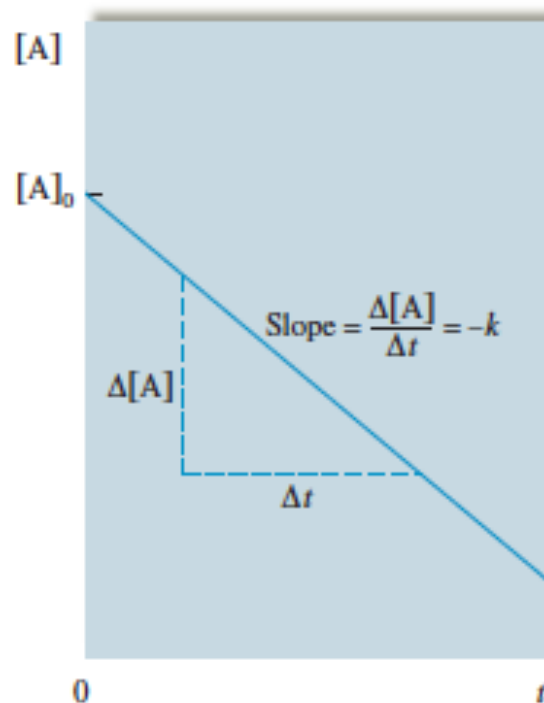
The integrated rate law for zero-order reaction is:

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

A plot of  $[A]$  versus  $t$ : is a straight line.

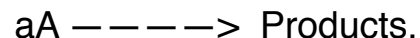
$$\text{Slope} = -k.$$

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





## First –Order Reactions (n = 1)



Doubling the concentration of A will double the rate of formation of the products.

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

Rate The integrated rate law is:

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

A plot of  $\ln[A]_t$  versus  $t$  is a straight line.

$$\text{Slope} = \text{change in } y / \text{change in } x = \Delta y / \Delta x = -k.$$

Half life is constant and does not depend on the concentration;  $t_{1/2} = 0.693/k$

**Example:**



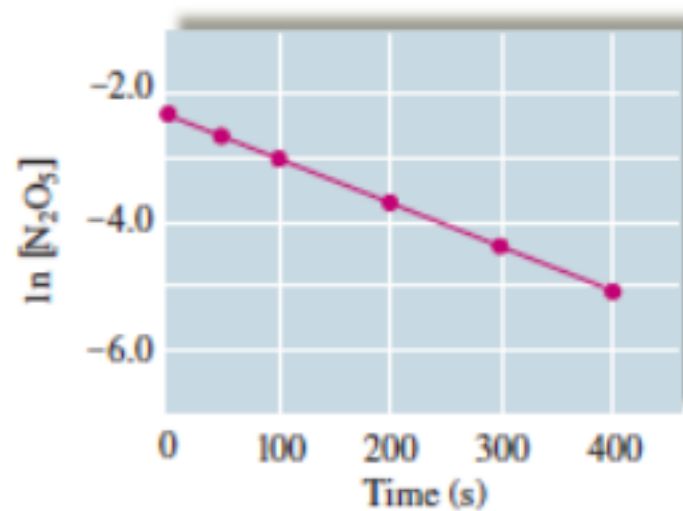
$[\text{N}_2\text{O}_5]$	Rate (mol/L · s)
0.90 M	$5.4 \times 10^{-4}$
0.45 M	$2.7 \times 10^{-4}$

Doubling the concentration doubles the rate of formation of the products.

A plot of  $\ln[A]_t$  versus  $t$  is a straight line. Slope =  $-k = -5.075 - (-2.303) / 400 - 0 = -6.93 \times 10^{-3} \text{ s}^{-1}$

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

$\ln[\text{N}_2\text{O}_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400



Two ways to determine half life of first order.

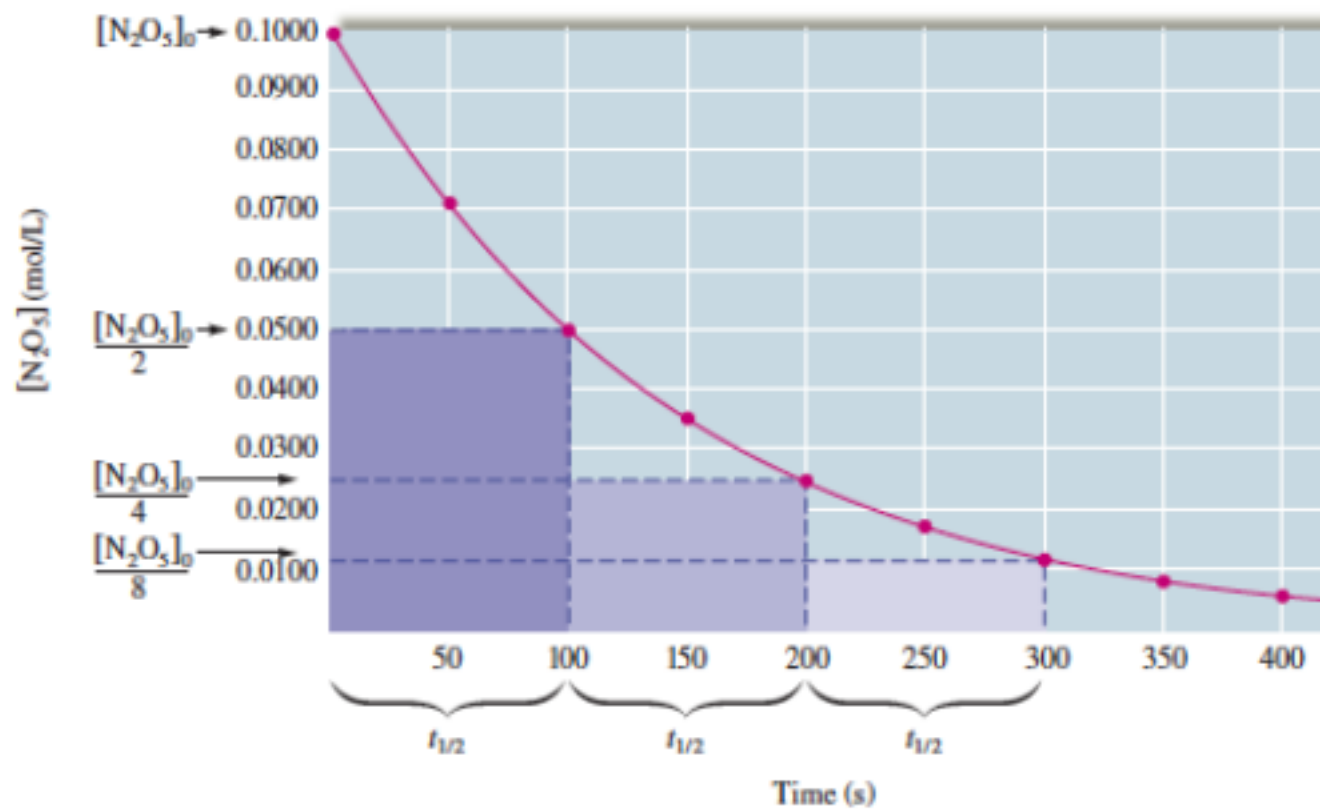
**Way one: Using the table data**

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

$[\text{N}_2\text{O}_5]$ (mol/L)	$t$ (s)	
0.100	0	$\left. \begin{array}{l} \Delta t = 100 \text{ s;} \\ \frac{[\text{N}_2\text{O}_5]_{t=100}}{[\text{N}_2\text{O}_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2} \end{array} \right\}$
0.0500	100	
0.0250	200	$\left. \begin{array}{l} \Delta t = 100 \text{ s;} \\ \frac{[\text{N}_2\text{O}_5]_{t=200}}{[\text{N}_2\text{O}_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2} \end{array} \right\}$
0.0125	300	

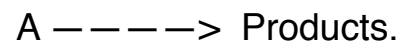
When the concentration of the reactant decreases by  $\frac{1}{2}$ , the time intervals, namely  $t_{1/2}$  remains the same (100s). In other words, every 100s, the concentration decreases by half.

Way two: Using the graph.



When the concentration of the reactant decreases by  $\frac{1}{2}$ , the time intervals, namely  $t_{1/2}$  remains the same (100s). In other words, every 100s, the concentration decreases by half.

## Second-Order Rate Laws (n = 2)



When the concentration of A is doubled, the rate of formation of the product will be multiplied by 4.

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

The integrated rate law is

$$1/[A]_t = k t + 1/[A]_o$$

A plot  $1/[A]_t$  of versus t: is a straight line. Slope = k .

Intercept =  $1/[A]_o$

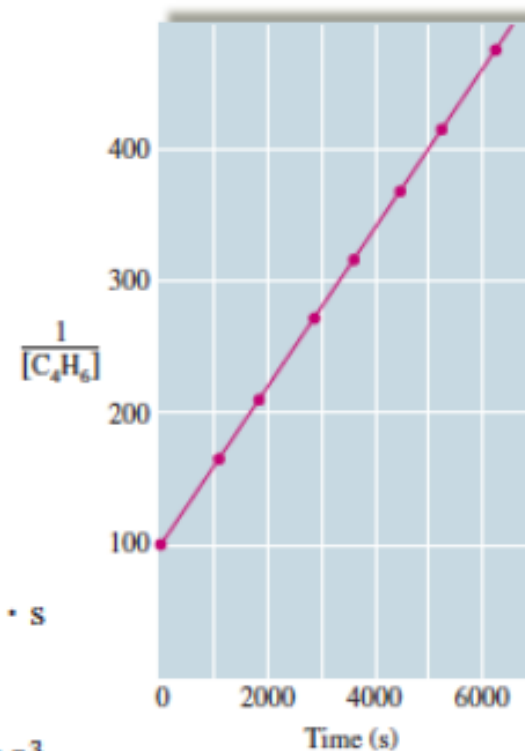
$$\text{Half life: } t_{1/2} = 1/k [A]_o$$

## Example



$[\text{C}_4\text{H}_6]$ (mol/L)	Time ( $\pm 1$ s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

$t$ (s)	$\frac{1}{[\text{C}_4\text{H}_6]}$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175



$$k = \text{slope} = \frac{(481 - 100) \text{ L/mol}}{(6200. - 0) \text{ s}} = \frac{381}{6200.} \text{ L/mol} \cdot \text{s} = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{ s}$$

$$\text{Rate} = k [\text{C}_4\text{H}_6]^2$$