

## Chemical Kinetics 2

Reading: Ch 13 sections 3-4

Homework: Chapter 13: 33, 35\*, 37, 39\*, 41\*, 43, 47\*, 49\*, 51\*

\* = 'important' homework question



*Either* the concentration of reactants *or* the temperature at which a reaction occurs is typically varied when performing kinetic studies.

*Concentration* (the rate equation / initial rate method) and *temperature* effects (the Arrhenius equation) will be covered separately in 'Chemical Kinetics 2' & 'Chemical Kinetics 3', respectively.

### Concentration and Rate – The Initial Rate Method

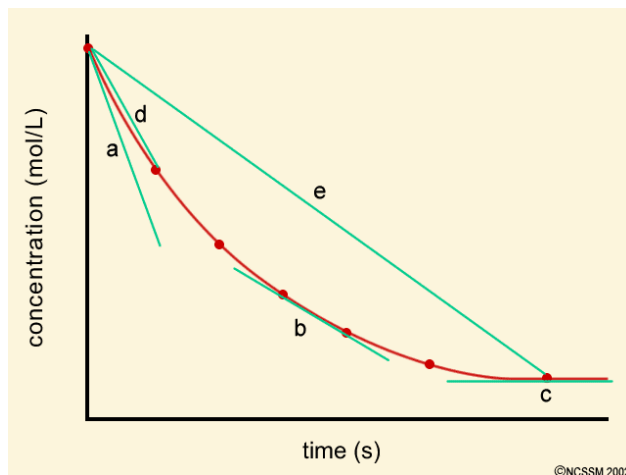
Recap: What happens to the rate of any reaction when [reactants] is increased? What fundamental *microscopic* events lead to this *macroscopic* observation?



Overview: The initial rate method involves measuring the initial rate of reaction (gradient of the [conc] v time plot at  $t=0$ ) of *either* the disappearance of reactant(s) *or* the initial rate of appearance of product(s) *for a set of experiments featuring reactants of various starting concentrations.*

This data allows for the determination of the Rate Law Equation (discussed below). **Determining the Rate Law Equation is the primary objective of most kinetic studies.**

Recall: Generic Graph of Concentration *Reactant* v Time for a chemical reaction:



The *initial rate* of reaction ((a), gradient of the curve at  $t=0$ ) is typically extrapolated. In contrast, *instantaneous rates* (b), (c) and (d) are calculated via the graphical and/or tabular methods discussed in 'Chemical Kinetics 1'. Therefore:

The *INITIAL RATE*  $\approx$  the *INSTANTANEOUS RATE* at  $t=0$

### Determining the Rate Law

#### Discussion:

How would you expect the initial rate of reaction of any chemical process to vary with the concentration of the reactants? Express this with an equation.

Would you expect all of the reactants to be equally important with regard to the overall rate of reaction? Express this with an equation.



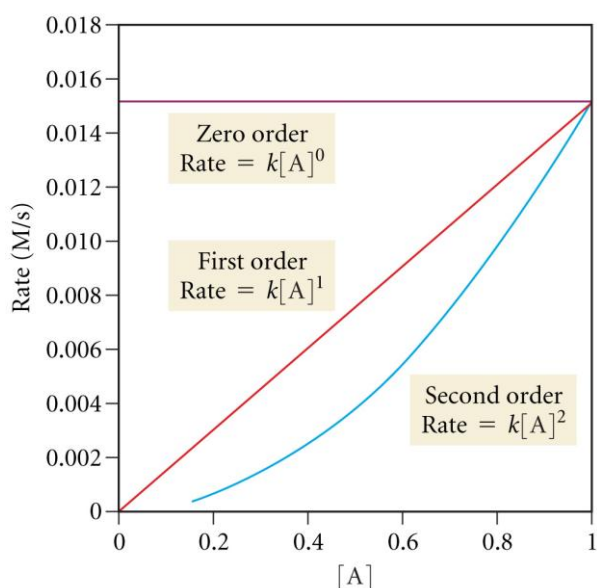
A chemical equation and its respective rate law equation are related via the following generic expression:



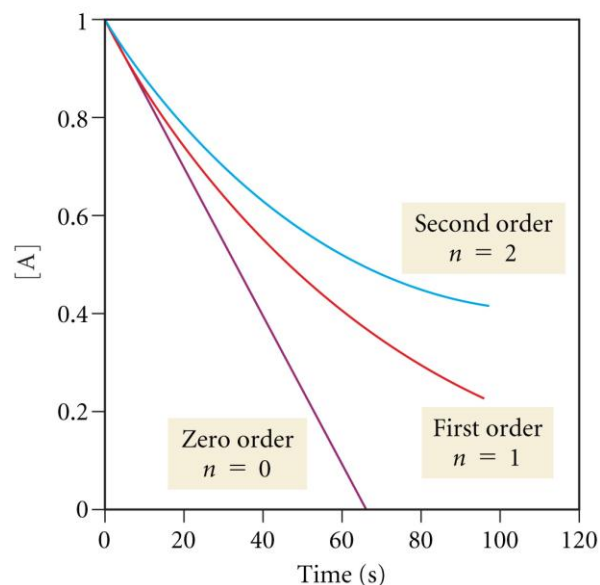
$$\text{Rate} = k[A]^m[B]^n$$

### Graphical Examples (details later)

Rate versus Reactant Concentration



Reactant Concentration versus Time



Where:

$$\text{(initial) rate of reaction} = \frac{\Delta [\text{Chemical}]}{\Delta t}$$

$k$  = Rate constant – determined from initial rate data

$[A], [B]$  = Reactant concentrations

$m, n$  = *Experimentally determined* (from initial rate data) reactant ‘orders’. The stoichiometric constants ( $a, b$  etc) are **not** the same as the order determined for their respective concentrations (e.g.  $[A]^m, [B]^n$ ) although they may **coincidentally** have the same numerical value (0, 1 or 2)



**The Rate Law is an equation that relates the rate of reaction to the [reactant(s)] raised to various powers ([reactant(s)]<sup>n</sup>).**

**The power to which each [reactant] is raised is known as its 'order'. The larger the order, the more the [reactant] influences the overall rate of reaction**

**Orders values are typically determined to be 0, 1, or 2. Non-integer values are occasionally encountered, but this is rare**

**The rate law can only be determined through initial rate data obtained experimentally**

Worked Example:

For the reaction:  $A + B \rightarrow C$ , the following data was obtained experimentally:

<u>Experiment#</u>	<u>[A]</u>	<u>[B]</u>	<u>Initial rate (M/s)</u>
1	0.100	0.100	$4 \times 10^{-5}$
2	0.100	0.200	$4 \times 10^{-5}$
3	0.200	0.100	$16 \times 10^{-5}$

- Find:
- The rate law expression for this process
  - The numerical value and units of the rate constant,  $k$
  - The rate of reaction when  $[A] = 0.05M$  and  $[B] = 0.10M$



*'Right off the bat'* - by looking at the table, which reactant has the biggest affect on the initial rate of reaction?

Which reactant has no affect on the initial rate of reaction?

What does this mean in terms of what's happening on the microscopic level?

Game Plan: Assume Rate =  $k[A]^m [B]^n$ , then:

1.	Determine the values of $m$ and $n$ through ‘observation’ (easy problems) or by manipulating rate law expressions for specific experimental sets – ‘math’ method
2.	Find $k$ via ‘insert and evaluate’ for an experimental data set
3.	Use the completed rate law expression to find reaction rate when $[A] = 0.05 \text{ M}$ and $[B] = 0.10 \text{ M}$

1. Finding the order of reaction with respect to each reactant

**To find the order of reaction for a reactant, two experimental data sets must be compared.** This can be done in either of two ways - via ‘Math’ or through simple ‘Observation’

A. ‘Mathematical’ Method for Determination of Reaction Orders



**Substitute values of [reactant] and initial rate directly into the respective rate expressions for a pair of experimental data sets (Note: the first data set is usually the ‘denominator’ – see below example)**

**Divide these two equations by one another to find the value of the order of reaction for a reactant.**

**Repeat the process for remaining data sets in order to determine each order of reaction for each reactant**

Walk through Recall that: Rate =  $k [A]^m [B]^n$  (*just substitute the numbers*)

(2)

(1)

Now, for the missing order, divide a pair of data sets where the required reactant's conc. is altered:

(3)

(1)

### B. 'Observation' Method for Determination of Reaction Orders



For easy numbers (like those in the example) simply use the following relationship for a pair of experimental data sets:

$$(\text{Factor [reactant] is multiplied})^{\text{order wrt that reactant}} = \text{Factor rate is multiplied}$$

Note: This method ONLY works if one [reactant] is varied (by an integer multiple) with all other [reactant(s)] remaining fixed.

e.g: For experiments (1) and (3)

[A] is doubled, while [B] remains constant. The rate increases by a factor of x4 between the two data sets ( $4 \times 10^{-5}$  M/s compared to  $16 \times 10^{-5}$  M/s)

Therefore:

$$2^m = 4$$

Question: What is the value of  $m$ , i.e. the order wrt [A]?

Answer:

Task: Analyze data sets 1 and 2, determine the order of reaction wrt [B]

The 'orders' can now be included in the rate law expression:

$$\text{i.e. Rate} = k[\text{A}]^2[\text{B}]^0$$

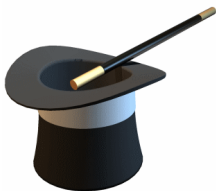
The reaction is said to be 'second order wrt **A**' and 'zero order wrt **B**'

Discussion: What does this statement mean in terms of how each reactant affects the overall rate of reaction? Recall previous graphs.

The reaction is said to be 'second order overall'.

Discussion: How is the overall rate of reaction related to the individual orders of reaction for each reactant?

## 2. Finding the numerical value and units of $k$ (the rate constant)



**A. Substitute values of initial rate, [reactant(s)] and respective order(s) from any experimental data set into the rate expression.**

**B. Rearrange the equation obtained to make  $k$  the subject. Solve for  $k$ . Keep the units of each quantity in the equation – these will determine the units of  $k$**

Note: Since the order of reaction wrt **B** is zero it can now be excluded from the rate expression. Why?

$$\text{rate} = k [\text{A}]^2$$

$$k = \frac{\text{rate}}{[\text{A}]^2}$$

Substituting values from Experiment #1(line 1):

$$\begin{aligned} k &= \frac{4.0 \times 10^{-5} \text{ M/s}}{[0.100\text{M}]^2} \\ &= \underline{4.0 \times 10^{-3} \text{ M}^{-1}/\text{s}} \end{aligned}$$



UNITS:

The units of  $k$  depend on those of the other variables – be sure to derive the units of  $k$  work them out each time you find its numerical value



3. Use the completed rate law expression to find reaction rate for defined values of [A] and [B]



The complete *quantitative* form of the rate equation can now be written out – simply substitute values for  $k$  and the orders wrt each reactant into the equation's generic form:

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

$$\text{Rate} = 4.0 \times 10^{-3} \text{ M}^{-1}/\text{s} [\text{A}]^2$$

Task: Determine the rate of reaction when [A] = 0.05 M and [B] = 0.10 M

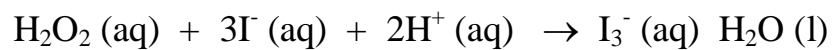


The rate of reaction for any condition of [reactant(s)] can be determined from the quantitative form of the rate equation - simply 'insert and evaluate'.

Note: Recall that the units of reaction rate are *always* M/s

$$\text{ANS} = 1.0 \times 10^{-5} \text{ M/s}$$

Task: Determine the quantitative rate law expression, including the numerical value of k, for the following process:



Initial rate data:

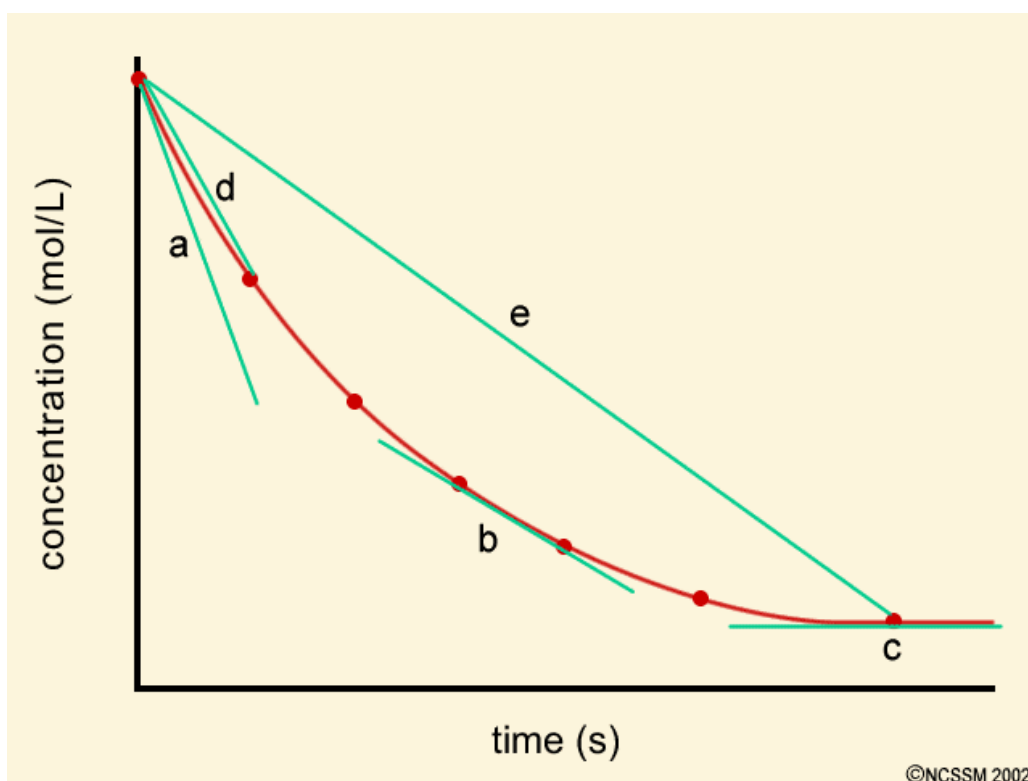
Experiment	[H <sub>2</sub> O <sub>2</sub> ]	[I <sup>-</sup> ]	[H <sup>+</sup> ]	Initial rate (M/s)
1	0.01	0.01	0.0005	1.15 x10 <sup>-6</sup>
2	0.02	0.01	0.0005	2.30 x10 <sup>-6</sup>
3	0.01	0.02	0.0005	2.30 x10 <sup>-6</sup>
4	0.01	0.01	0.0010	1.15 x10 <sup>-6</sup>

Recall: rate = k [H<sub>2</sub>O<sub>2</sub>]<sup>m</sup>[I<sup>-</sup>]<sup>n</sup>[H<sup>+</sup>]<sup>p</sup>, so values for each order (n, m and p) must be determined.

## Concentration and Rate – Integrated Rate Law Expressions

Recap: The *initial*, *average* and/or '*instantaneous*' rate(s) of reaction are calculated by finding the gradient of the experimentally determined [conc.] v time plot by either:

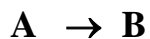
1. Finding the gradient of a tangent line applied to the data at the point of interest *or*
2. Finding the gradient between a pair of data points straddling the point of interest



Recall: initial rate and [reactant] data acquired for a series of experimentally determined [conc.] v time plots are utilized in the determination of the reaction's respective rate law expression:



Discussion: Consider the following simple, generic decomposition reaction:

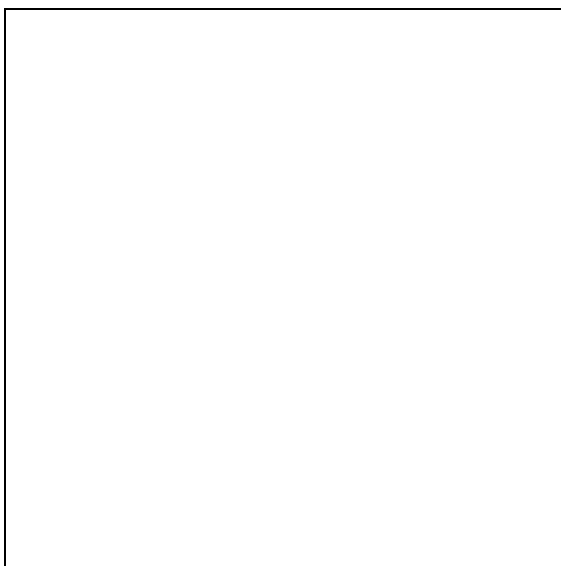


For such a reaction, which is typically either first or second order, the following respective rate expressions would apply:

1<sup>st</sup> order rxn: **Rate** =  $k[\mathbf{A}]^1$       2<sup>nd</sup> order rxn: **Rate** =  $k[\mathbf{A}]^2$

Which reaction would proceed at a faster rate (assuming  $k$  was similar in each case) – the 1<sup>st</sup> or 2<sup>nd</sup> order process? Why?

In the boxes below, sketch simple [reactant] v time plots for chemical processes that are 1<sup>st</sup> and 2<sup>nd</sup> order *overall*, respectively. Recall previous slides.



**First order overall**



**Second order overall**



First order processes have '*shallow*' rate of reaction curves

Second order processes have '*steep*' rate of reaction curves

Discussion: Which mathematical functions (when graphed) have similar features to the first and second order rate of reaction curves?



**First and second order reaction processes may be described by  $y = e^{-x}$  and  $y = 1/x$  functions, respectively**



**Linear ( $y = mx + b$ ) versions of either the first or second order rate plots may be obtained through integration of their respective line-shapes.**

These important results yield equations that allow  $k$  and [reactant] to be found at **any** time during the reaction

### **Integrated Rate Equation for 1<sup>st</sup> Order Reactions**

Process:  $A \rightarrow B$

$$\text{Rate} = \frac{-\Delta [A]}{\Delta t} = k[A]^1$$

Derivation:

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

Interpretation:

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

$$y = mx + b$$

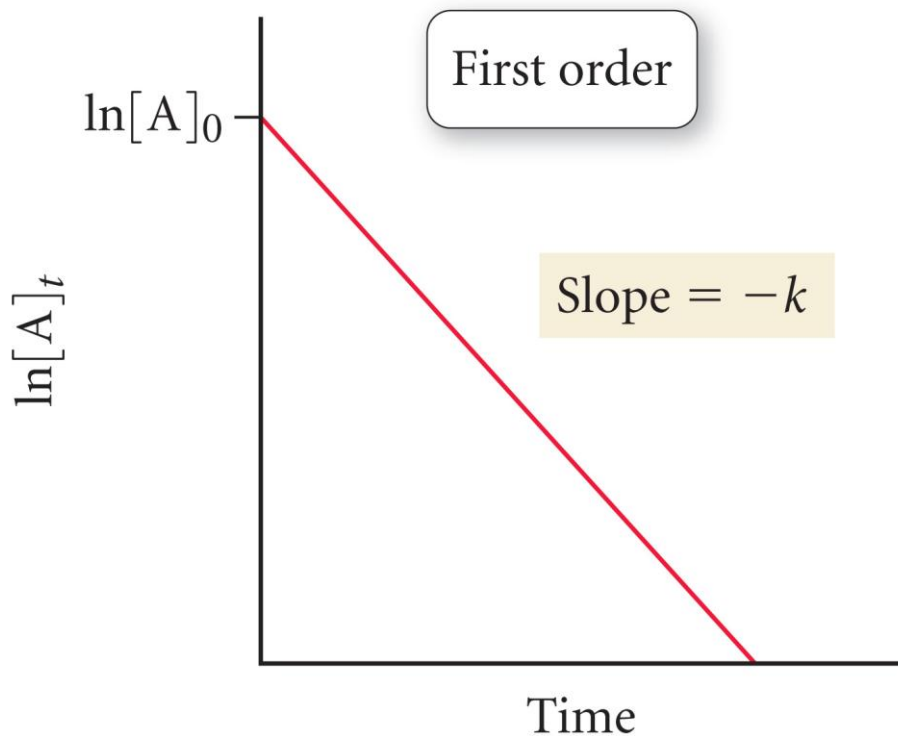


A plot of  $\ln$  (or  $\log_{10}$ ) [reactant] v time will yield a **LINEAR** plot for a 1<sup>st</sup> order process.



The plot will have a slope of  $-k$  and an intercept of  $\ln[A]_0$  (natural log of [reactant] at  $t=0$ )

Generic Graph



Example (p581 & appendix): the decomposition of  $\text{SO}_2\text{Cl}_2$

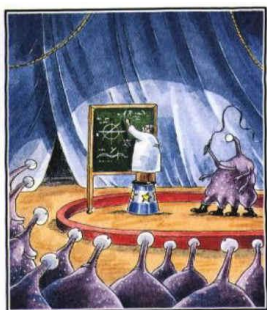


## Integrated Rate Equation for 2<sup>nd</sup> Order Reactions

Process:  $A \rightarrow B$

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

Derivation:



Abducted by an alien circus company, Professor Doyle is forced to write calculus equations in center ring.

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

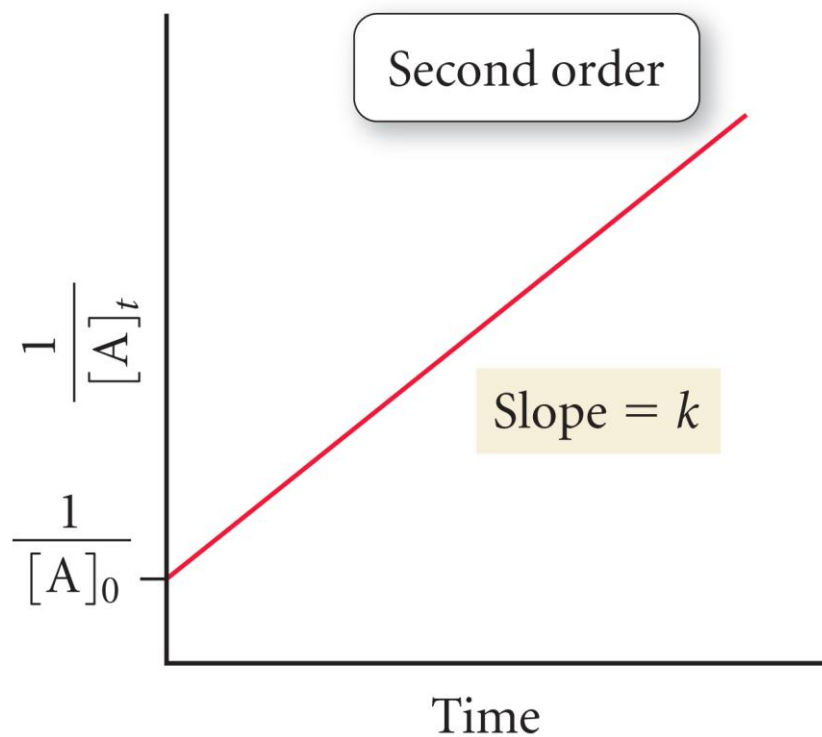
Interpretation: 
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
  
$$y = mx + b$$



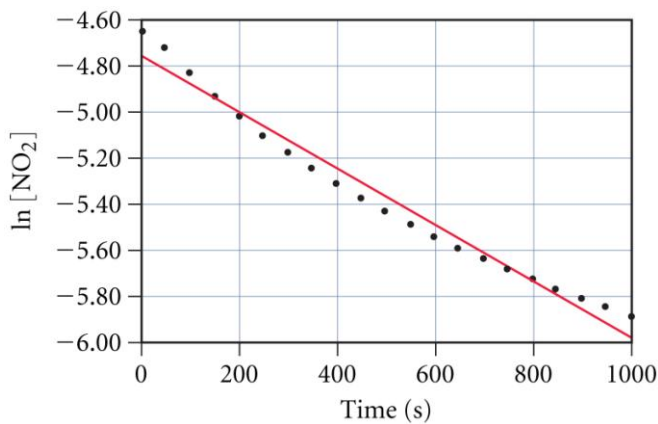
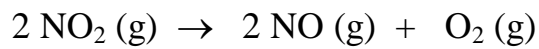
A plot of  $1/[\text{reactant}]$  v time will yield a **LINEAR** plot for a 2<sup>nd</sup> order process.

The plot will have a slope of  $k$  and an intercept of  $1/[A]_0$  (reciprocal of [reactant] at  $t=0$ )

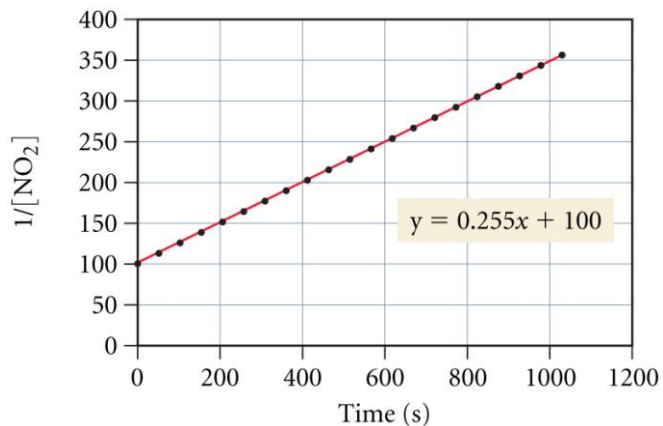
## Generic Graph



Example (p 583 & appendix): experimental data for the decomposition of nitrogen dioxide



1st order plot is non liner – *reject*



2<sup>nd</sup> order plot is liner – *'good to go'!*



Worked Example: For the reaction:



The following data was acquired via an initial rates experimental analysis:

$$\text{Rate} = k [\text{N}_2\text{O}_5]^1, \text{ where } k = 4.8 \times 10^{-4} \text{ s}^{-1}$$

Task: If the initial concentration of dinitrogen pentoxide is  $5.0 \times 10^{-3} \text{ M}$ , what is this reactant's concentration after 625 seconds?

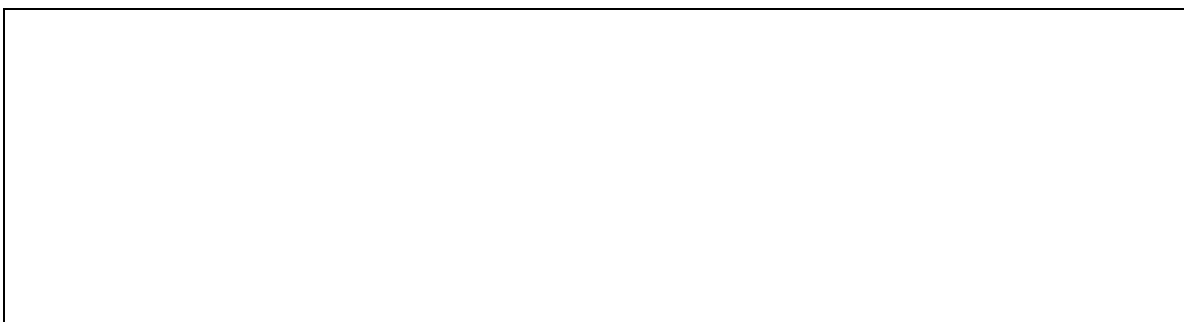
Discussion: How would you solve this problem (there are two methods)?

Plan and execution:

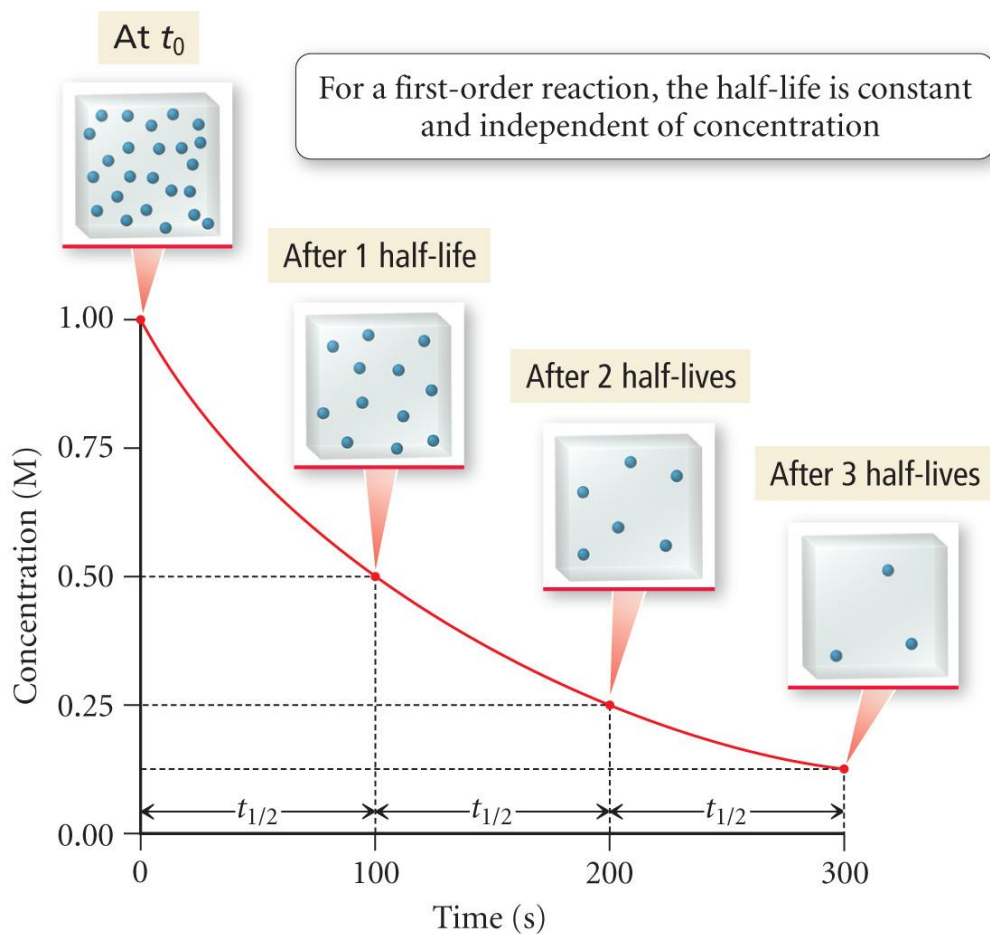
ANS:  $3.7 \times 10^{-3} \text{ M}$

## Reaction Half-Life

Discussion: What do you understand by the phrase 'half-life'?



Relationship between [reactant] and time for 1, 2 and 3 half-lives



## Half-life expressions



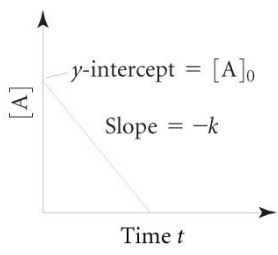
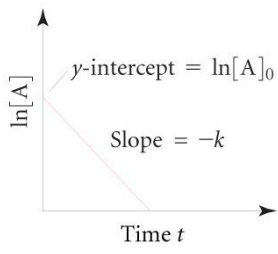
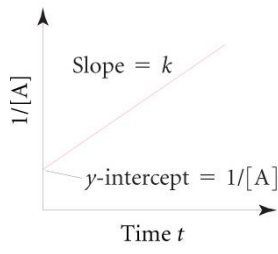
**By definition, the [reactant] ( $[A]_t$ ) is exactly half its initial value ( $[A]_0$ ) after one half-life for any reaction.**

This fact allows for relationships between half-life ( $t_{1/2}$ ),  $k$  and (for second order processes)  $[A]_0$  to be determined

Derivation: 1<sup>st</sup> order reactions

Task: Derive an expression for the half-life of a 2<sup>nd</sup> order process in terms of  $k$  and  $[A]_0$

Summary: (p 587 & appendix)

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

Example: For the reaction:



Assuming the reaction is first order overall and  $k = 2.20 \times 10^{-5} \text{ s}^{-1}$ , then:

1. What is the half-life of  $\text{SO}_2\text{Cl}_2 (\text{g})$ ?
2. How long would it take for 50% of the sample to decompose?
3. How long would it take for 75% of the sample to decompose? Trick??



*“Standard question”*

The following question is a great example of the type asked on standardized tests like the MCAT etc. As is often the case, once you know the trick they are easy....

Question (14.19)

For the reaction:  $A + B \rightarrow C$

The rate equation has the form:  $\text{rate} = k [A]^x$ . What is the value of x if:

- a. The rate triples when [A] triples?
  
  
  
  
  
  
  
  
  
  
- b. The rate increases eightfold when [A] is doubled?
  
  
  
  
  
  
  
  
  
  
- c. There is no change in rate when [A] is tripled?

Discussion: What is the ‘trick’ (i.e. what underlying theory is being tested?)



### “Initial rates”

The following question was taken from your 1<sup>st</sup> practice midterm:

Consider the generic reaction:



Assuming the above reaction was analyzed using the initial rate method at 25°C, use the data below to determine:

1. The order of reaction with respect to each reactant and the overall order of the reaction. **Summarize your findings in the form of a complete rate equation.**
2. The value of  $k$  at this temperature.
3. What is the rate of reaction when the concentrations of *each* reactant is 0.50 M,

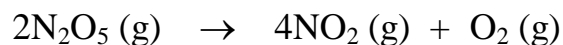
Experiment	Initial concentrations (molL <sup>-1</sup> )			Initial rate (molL <sup>-1</sup> s <sup>-1</sup> )
	A	B	C	
1	0.10	0.10	0.50	1.5 x 10 <sup>-6</sup>
2	0.20	0.10	0.50	3.0 x 10 <sup>-6</sup>
3	0.10	0.20	0.50	6.0 x 10 <sup>-6</sup>
4	0.10	0.10	1.00	1.5 x 10 <sup>-6</sup>



*“Half - life”*

The following question was taken from your 1<sup>st</sup> practice midterm:

Question 3a (10 points): The decomposition of  $\text{N}_2\text{O}_5$  (g) is a first order process:

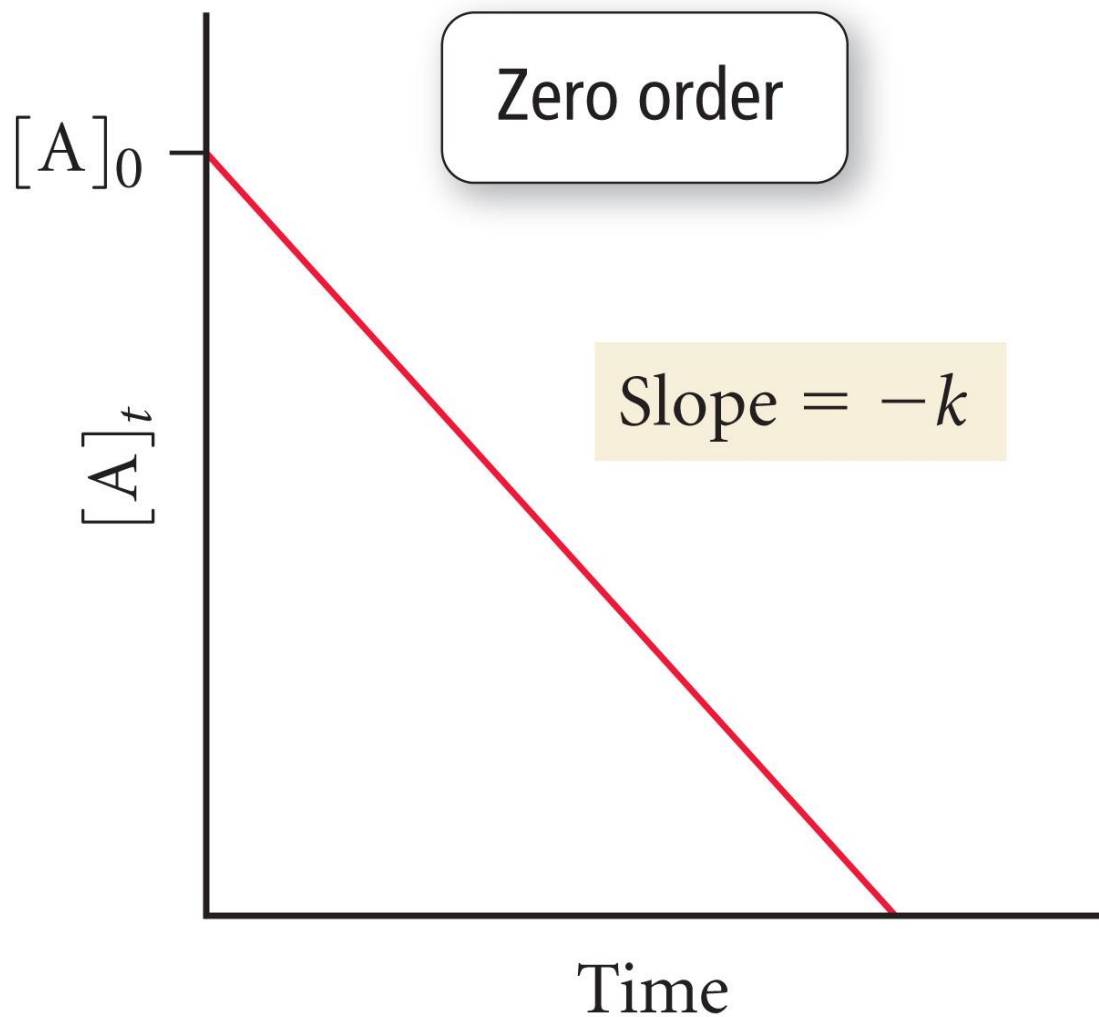


The concentration of  $\text{N}_2\text{O}_5$  (g) may be monitored with time using a simple diode colorimeter. If, during such an experiment,  $k$  is determined to be  $5.2 \times 10^{-4} \text{ s}^{-1}$ , then what is the half-life of the reaction measured in minutes?

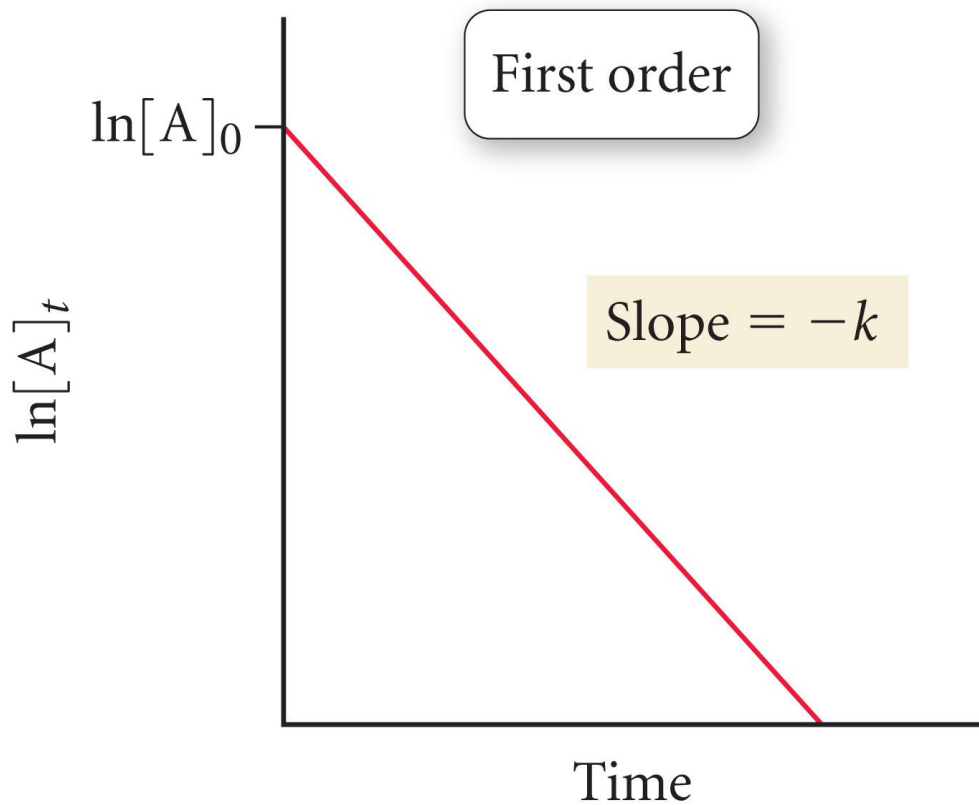
Question 3b (15 points): If, in the above experiment, an absorbance of 0.84 is recorded immediately prior to the commencement of  $\text{N}_2\text{O}_5$  (g) decomposition (i.e. at  $t = 0$ ), then what absorbance value will be recorded after exactly one half-life has passed? Recall that  $\text{Abs} \propto [\text{N}_2\text{O}_5]$

For the above reaction, what Abs value would be detected by the colorimeter after exactly three half-lives had passed?

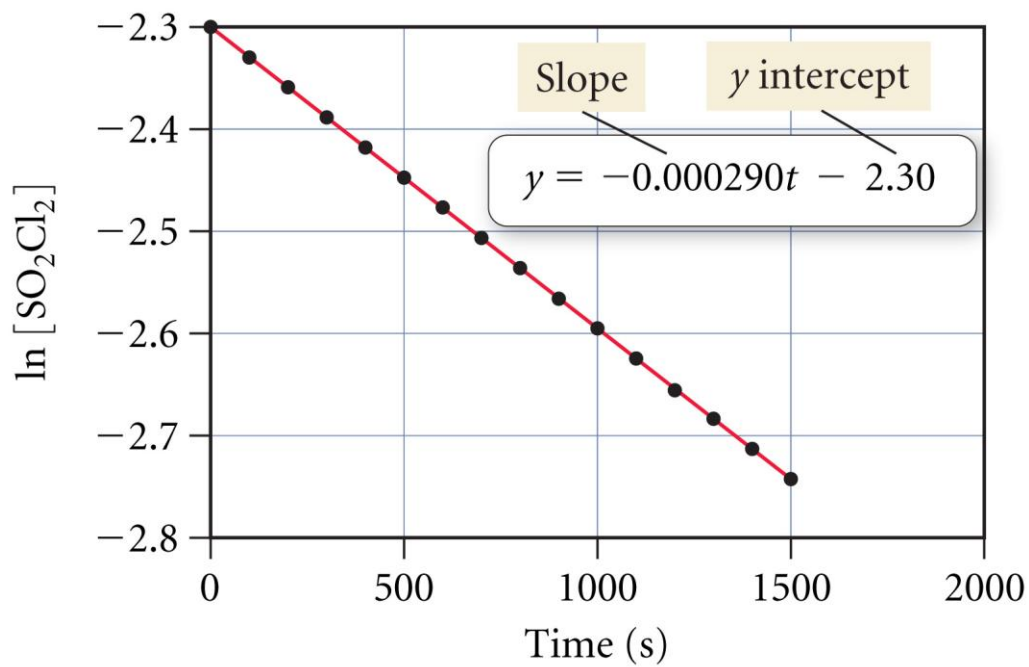
Appendix



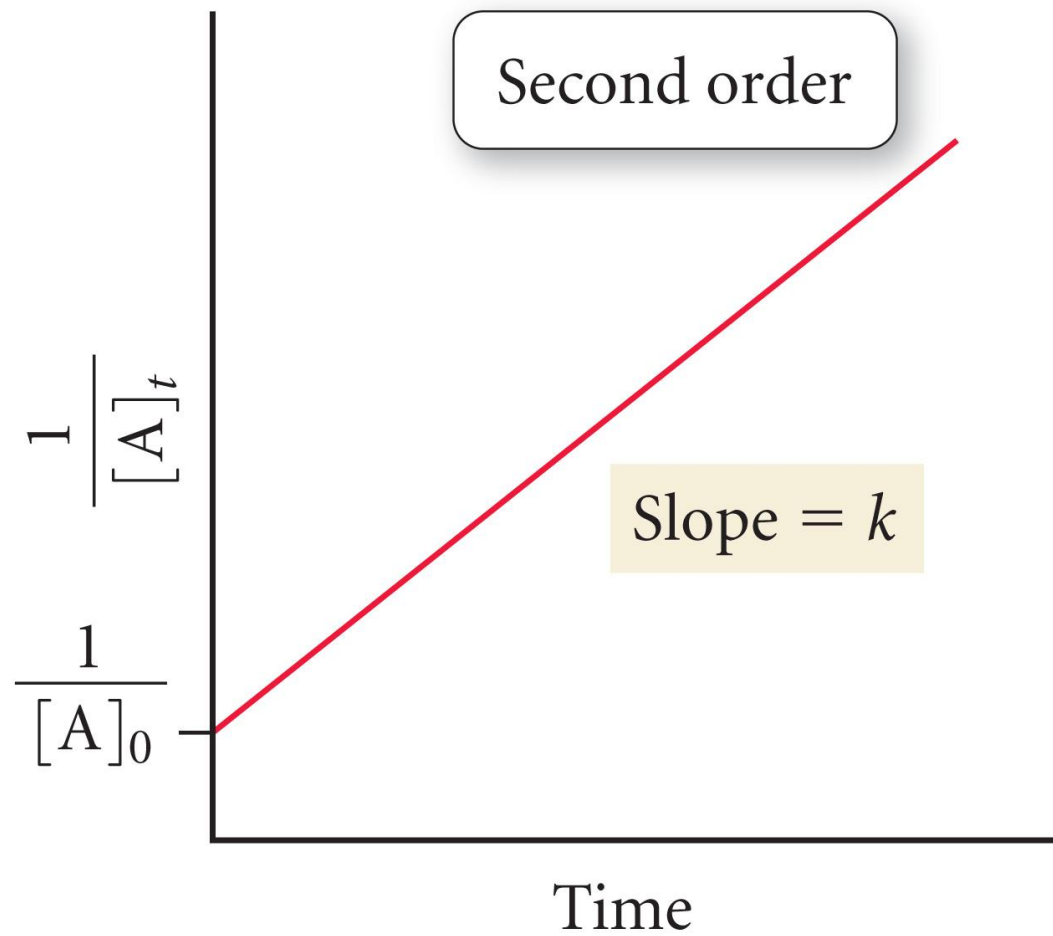


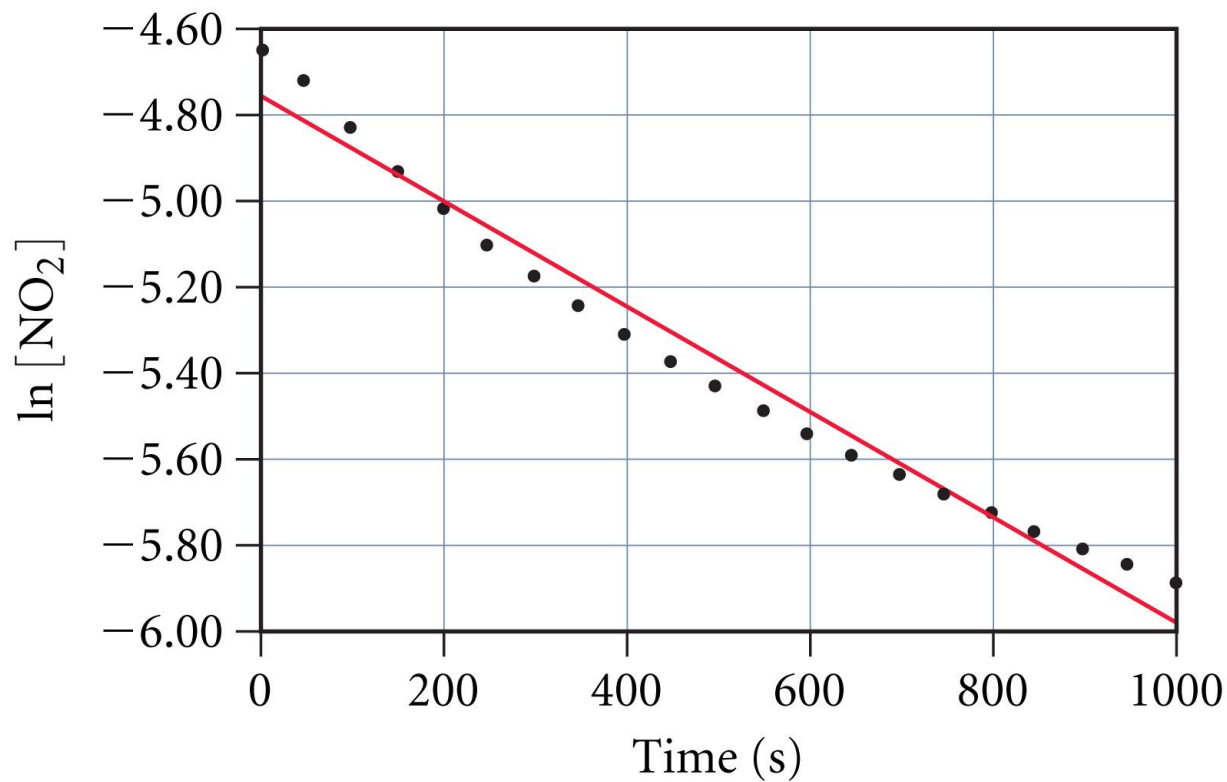


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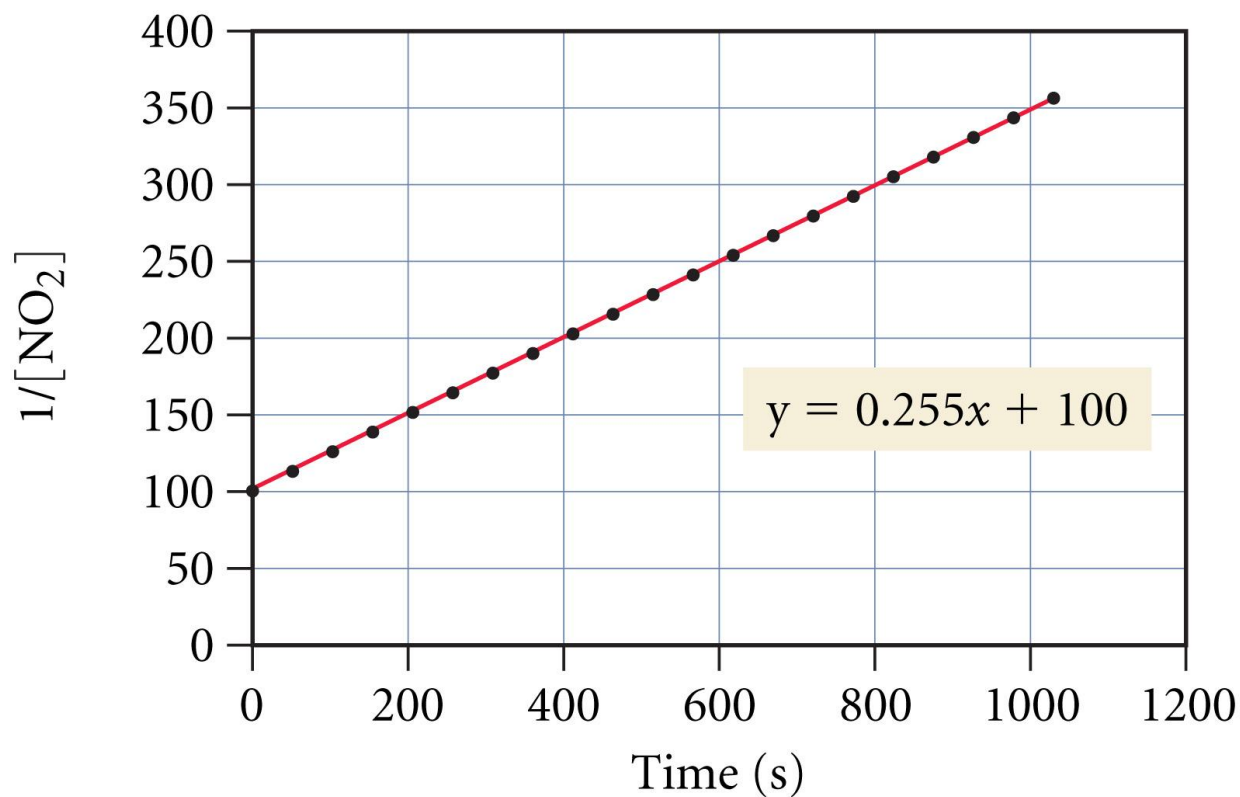


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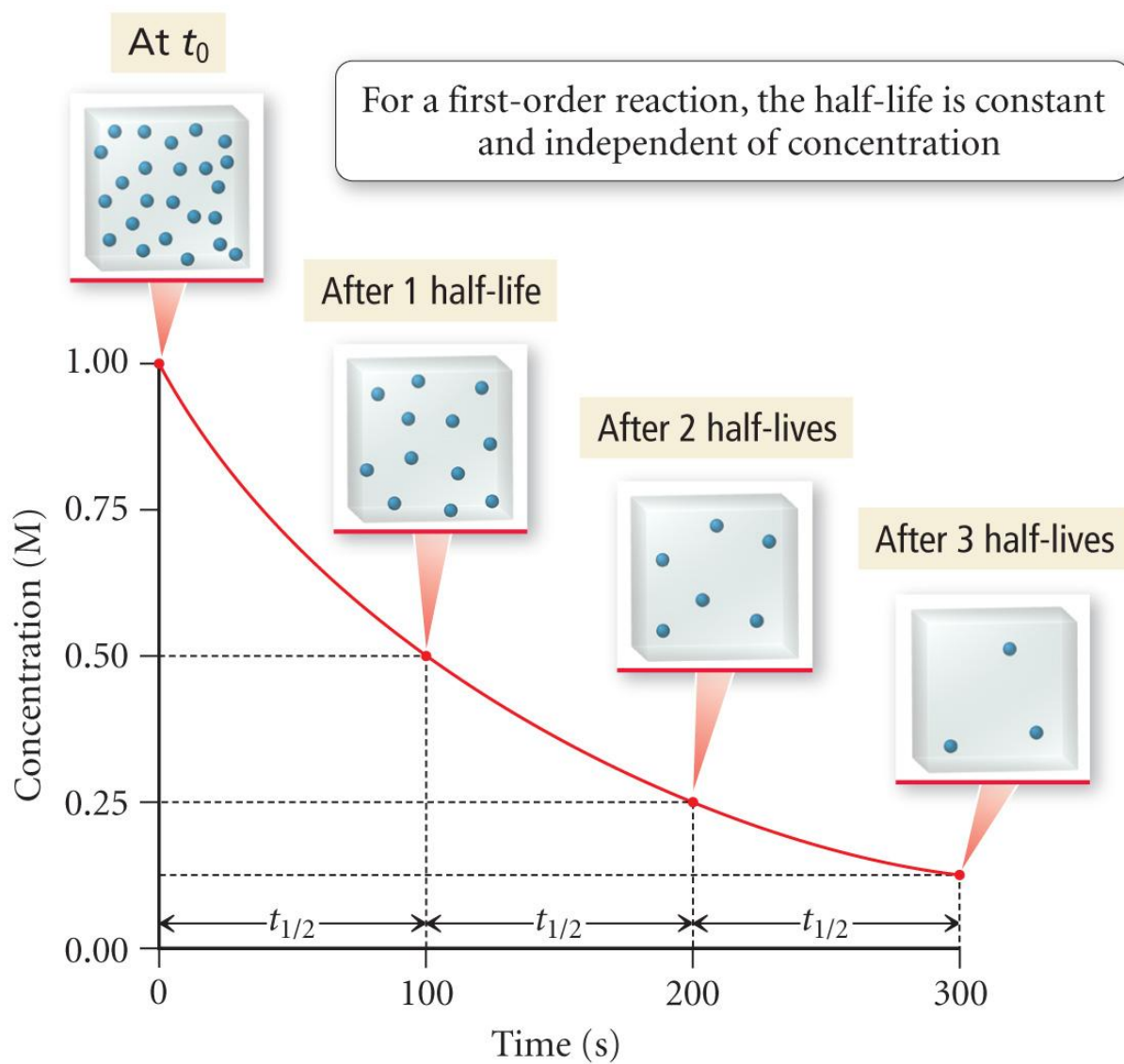


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## Half-Life for a First-Order Reaction



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**TABLE 13.2 Rate Law Summary Table**

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