

*ALE 3. Integrated Rate Laws*(Reference: *16.4 Silberberg 5<sup>th</sup> edition*)**How does reactant concentration change over time for 1<sup>st</sup> and 2<sup>nd</sup> order reactions?****The Model: The Integrated Rate Laws for 1<sup>st</sup>- and 2<sup>nd</sup>-Order Decompositions**

A common type of reaction is the decomposition of a single species (which is here generically labeled as “A”):



(Basically any stoichiometry is possible, as both sides of the chemical equation could be divided by the same constant to make the stoichiometric coefficient in front of A equal to 1.) We define the reaction rate in terms of the time rate of change of the concentration of A as:

$$\mathbf{rate = -\frac{\Delta[A]}{\Delta t}} \quad \mathbf{(1)}$$

If the decomposition reaction obeys first- or second-order kinetics, its rate law is:

$$\mathbf{Rate = -\frac{\Delta[A]}{\Delta t} = k[A]} \quad \mathbf{(2a)}$$

**1<sup>st</sup> order**

$$\mathbf{Rate = -\frac{\Delta[A]}{\Delta t} = k[A]^2} \quad \mathbf{(2b)}$$

**2<sup>nd</sup> order**Solving the differential equations 2a and 2b yields the **integrated rate laws**:

$$\mathbf{\ln[A]_t = -kt + \ln[A]_0} \quad \mathbf{(3a)}$$

**1<sup>st</sup> order**

$$\mathbf{\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}} \quad \mathbf{(3b)}$$

**2<sup>nd</sup> order**where  $k$  is the rate constant of the reaction,  $t$  is the amount of time that has elapsed from an initial time,  $[A]_0$  is the initial concentration, and  $[A]_t$  is the concentration of the decomposing species at time  $t$ .**Key Questions**

- Compare the general form of a linear equation ( $y = mx + b$ ) to the integrated rate law of a first-order reaction and to the integrated rate law of a second-order reaction. Fill in the table below, identifying what corresponds to  $y$ , to  $m$ , and to  $b$  for each integrated rate law.

	$y$	$m$	$x$	$b$
1 <sup>st</sup> order			$t$	
2 <sup>nd</sup> order			$t$	

2. If one is unsure whether the decomposition of a species  $A \rightarrow \text{Products}$  obeys first- or second-order kinetics, it is possible to plot both  $\ln[A]$  versus time and  $1/[A]$  versus time. The plot that results in a more linear fit to the observed data serves as strong evidence as to which order the decomposition reaction is.
- Suppose the decomposition is 1<sup>st</sup> order with respect to A.
    - Then a plot of \_\_\_\_\_ versus  $t$  results in a straight line.
    - Is the plot's slope positive or negative? (Circle your choice.)
  - Suppose the decomposition is 2<sup>nd</sup> order with respect to A.
    - Then a plot of \_\_\_\_\_ versus  $t$  results in a straight line.
    - Is the plot's slope positive or negative? (Circle your choice.)
  - What is the physical significance of the plots' slopes? (*i.e.*, What about the reaction that is investigated is learned by evaluating the slope of one of these plots?)

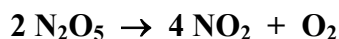
### Exercise

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3. Of the following decomposition reactions



and

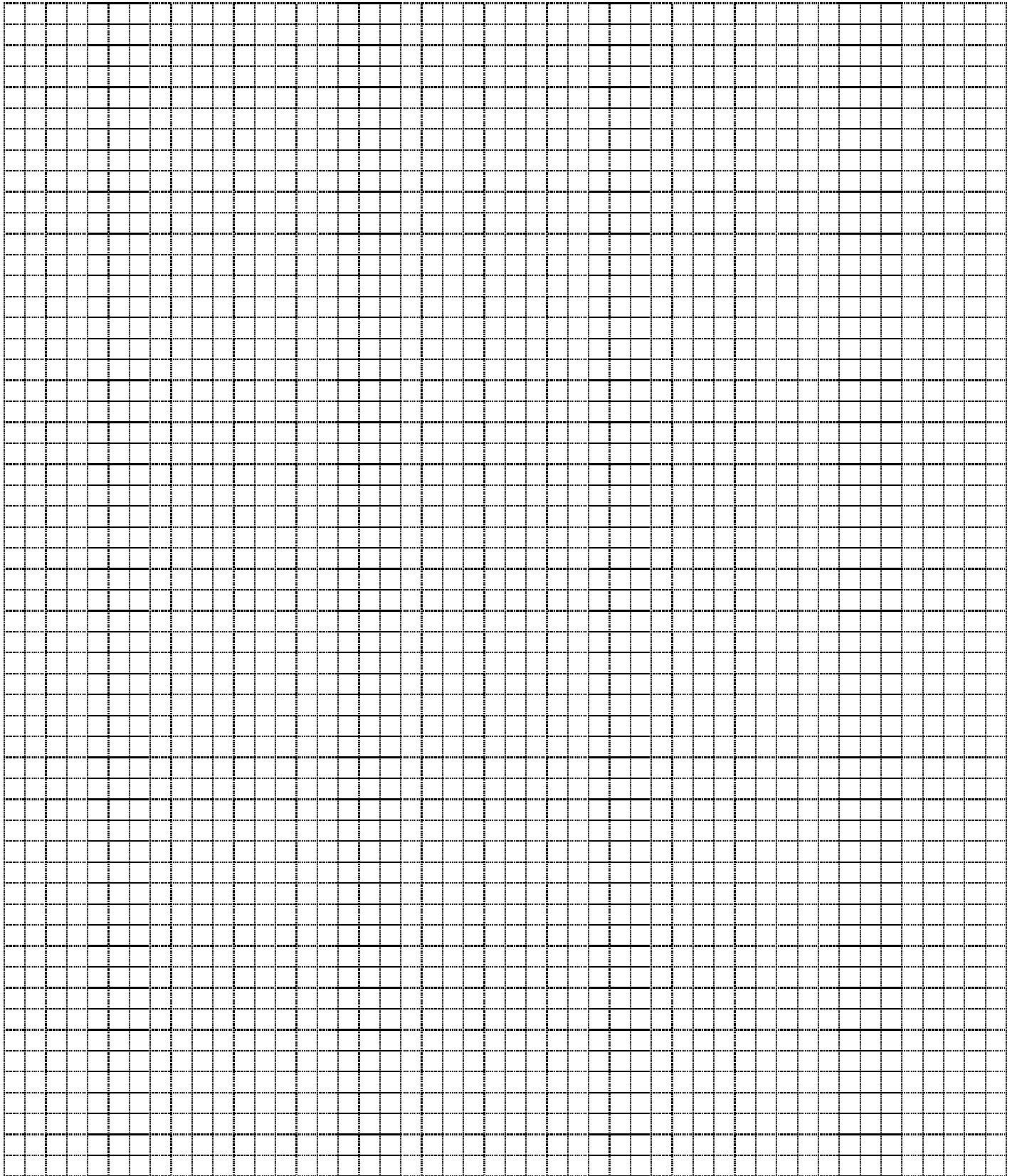


*one of them obeys first-order kinetics and the other obeys second-order kinetics.* Plot the following data to determine which substance ( $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$  or  $\text{N}_2\text{O}_5$ ) decomposes according to first-order kinetics and which one decomposes according to second-order kinetics. You may plot the data using *Excel* or by hand using the grid on the next page. If you plot the data by hand, before you plot the points it is best to first determine the maximum and minimum values on the  $y$ -axis and expand the scale to use as much of the grid as possible. If you don't, then you may not be able to tell which plot is most linear. If you use Excel, print your graph(s) showing the  $R^2$  value for each curve and tape each plot to the next page.

$t$ (s)	0	1000.	5000.	12000.
$[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}]$ (M)	0.250	0.161	0.067	0.033
$[\text{N}_2\text{O}_5]$ (M)	2.00	1.97	1.83	1.65

Which reaction obeys 1<sup>st</sup>-order kinetics? 2<sup>nd</sup>-order kinetics? Justify your response.

### Plots for Exercise #3



## The Model: Half-lives

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The **half-life** of a reaction is the amount of time required for one-half of the starting number of molecules to react (or decompose in the case of a decomposition reaction). Thus, at the half-life:

$$[\text{A}]_{t_{1/2}} = 0.5[\text{A}]_0$$

where the subscript  $t_{1/2}$  signifies that the concentration is at the half-life. The first order integrated rate law is  $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$  (eqn 3a). Therefore, if the reaction occurs through first-order kinetics:

$$\ln[\text{A}]_{t_{1/2}} = -k t_{1/2} + \ln[\text{A}]_0 \quad (4)$$

Substitution of the concentration at the half-life for the initial concentration yields:

$$\ln(0.5[\text{A}]_0) = -k t_{1/2} + \ln[\text{A}]_0$$

Using the rule  $\ln(ab) = \ln(a) + \ln(b)$  for handling logarithms yields:

$$\ln(0.5) + \ln[\text{A}]_0 = -k t_{1/2} + \ln[\text{A}]_0$$

Using the rule  $\ln(1/x) = -\ln(x)$  and simplification yields:  $kt_{1/2} = \ln(2)$  or  $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$  (5)

Thus, for a first-order reaction, if the rate constant is known, then the half-life of the reaction is also known (and vice versa).

### Key Questions

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- In a similar manner as was just shown in the Model for a first-order reaction, step-by-step derive the relationship between the rate constant and the half-life for a second-order reaction. (Do not just look it up, although you may do that to confirm you've derived the relationship correctly.)
- How does the initial reactant concentration affect the half-life of first- and second-order chemical reactions? (Hint: examine [eqn 5](#) and your answer to [question 4](#).)
  - Is the half-life of a first-order chemical reaction constant over time? How about a second-order reaction? Explain.

## Exercises

6. The gas-phase dimerization reaction (*i.e.*, a reaction involving the combining of two like molecules) of butadiene has a rate constant of  $0.0071 \text{ M}^{-1} \text{ s}^{-1}$  at  $326 \text{ }^\circ\text{C}$ :  $2 \text{ C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g})$
- What is the order of the reaction? (Hint: Examine the units of the rate constant!)
  - When the concentration of butadiene is  $0.0169 \text{ M}$ , what is the half-life of the reaction at  $326 \text{ }^\circ\text{C}$ ? Show your work using units and sig. figs. Circle your answer.
  - Starting with a butadiene concentration of  $0.0169 \text{ M}$ , how much time is required for the concentration of butadiene to drop to  $0.0134 \text{ M}$ ? Show your work using units and sig. figs. Circle your answer.

## Summary of Zero-, first- and Second-Order Rate Laws

Reaction Order	Rate Law	Integrated Rate Law	Integrated Rate Law in the form $y = mx + b$	Half-life
Zero	$\text{Rate} = k$	$[A]_o - [A]_t = kt$	$[A]_t = -kt + [A]_o$	$t_{1/2} = \frac{[A]_o}{2k}$
1 <sup>st</sup>	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Ln} \frac{[A]_o}{[A]_t} = kt$	$\text{Ln}[A]_t = -kt + \text{Ln}[A]_o$	$t_{1/2} = \frac{\text{Ln}2}{k}$
2 <sup>nd</sup>	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$	$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$	$t_{1/2} = \frac{1}{k[A]_o}$

7. Referring to the table above, what is the order in a reactant if a plot of
- $\text{Ln} [\text{Reactant}]_t$  vs. time is linear? \_\_\_\_\_ What does the slope equal? \_\_\_\_\_ The y-intercept? \_\_\_\_\_
  - $[A]_t$  vs. time is linear? \_\_\_\_\_ What does the slope equal? \_\_\_\_\_ The y-intercept? \_\_\_\_\_
  - $1/[\text{Reactant}]_t$  vs. time linear? \_\_\_\_\_ What does the slope equal? \_\_\_\_\_ The y-intercept? \_\_\_\_\_

8. At 25°C, hydrogen iodide breaks down very slowly to hydrogen and iodine:  $\text{Rate} = k[\text{HI}]^2$ . The rate constant at 25°C is  $2.4 \times 10^{-21} \text{ L mol}^{-1}\text{s}^{-1}$ . If 0.0100 mol HI (g) is placed in a 1.0-liter container, how long will it take for 10.0% of the HI to react?—i.e. how long will it take for the concentration of HI to reach 0.00900 mol/L? Show your work using units and sig. figs. Circle your answer.
9. A decomposition reaction has a rate constant of  $.0012 \text{ yr}^{-1}$ .
- What is the order of this decomposition reaction? \_\_\_\_\_ order
  - What is the half-life of the reaction? Show your work using units and sig. figs. Circle your answer.
  - How long does it take for [reactant] to reach 22.3% of its original value? Show your work using units and sig. figs. Circle your answer.
10. The radioactive isotope  ${}^{40}_{19}\text{K}$  ( $t_{1/2} = 1.25 \times 10^9 \text{ yr}$ ) is commonly found in rocks where it gradually decays to form  ${}^{40}_{18}\text{Ar}$ . Suppose a volcanic eruption melts a large area of rock and all gases are expelled from the hot molten rock. After cooling  ${}^{40}_{18}\text{Ar}$  accumulates from the radioactive decay of the  ${}^{40}_{19}\text{K}$  initially present in the rock. When a piece of rock is analyzed it is found to contain 1.38 mmol of  ${}^{40}\text{K}$  and 1.14 mmol  ${}^{40}\text{Ar}$ . **How long ago did the rock cool?** Hints: i.) All radioactive decay occurs by first-order kinetics. ii.) First calculate the rate constant for the radioactive decay of  ${}^{40}\text{K}$ . iii.) Now use the integrated rate law to determine the time. iv.)  ${}^{40}\text{K}$  decays to form  ${}^{40}\text{Ar}$  in a 1 to 1 mole ratio (This is useful when finding the mmol of  ${}^{40}\text{K}$  initially present!) Show your work using units and sig. figs. Circle your answer.