

**Warm-Up**

The table presents data for the reaction:  $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$ . The temperature of the reaction is constant.

Exp.	Initial Concentration (M)		Initial Rate
	[NO]	[H <sub>2</sub> ]	$-\Delta[\text{NO}]/\Delta t$ (M/s)
1	0.60	0.10	$1.8 \times 10^{-3}$
2	0.60	0.20	$3.6 \times 10^{-3}$
3	0.10	0.60	$3.0 \times 10^{-4}$
4	0.20	0.60	$1.2 \times 10^{-3}$

A) Determine the order of the reaction with respect to each reactant and write the rate law expression for the above reaction system.

B) Calculate the value of k, the rate law constant.

C) Calculate the necessary [NO] to achieve a rate of  $8.0 \times 10^{-4}$  M/s when  $[\text{H}_2] = 0.35$  M.

D) What is the initial rate of production of  $\text{N}_2(\text{g})$  in trial #3?

So far, we've determined reaction order by comparing initial concentration and initial reaction rates. You can also determine the reaction order by monitoring the change in concentration of a reactant over time.

## Integrated Rate Laws: The Change of Concentration with Time

### I. First Order Reactions

- For a first-order reaction, the rate law can be written as follows: **rate =  $k$  [A]**
- From calculus, the following integrated rate law can be obtained:  **$\ln[A]_t - \ln[A]_0 = -kt$**

(a) Define the meaning of each the following terms in the integrated rate law:

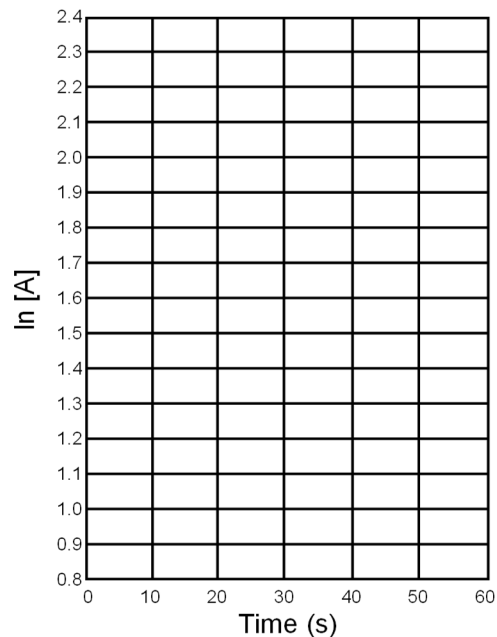
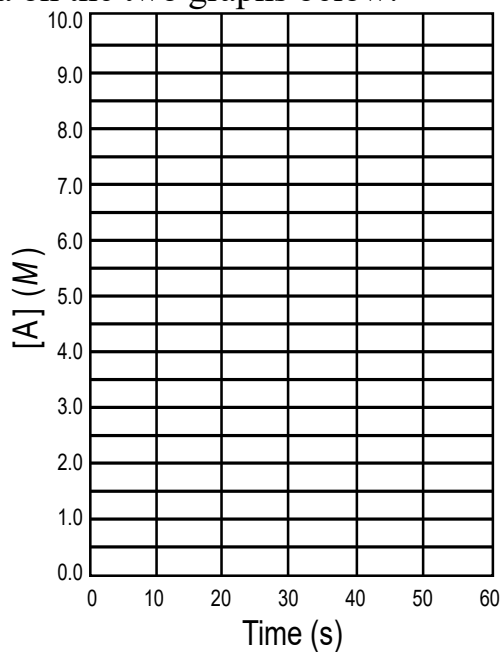
$[A]_0 =$  \_\_\_\_\_  $[A]_t =$  \_\_\_\_\_  $k =$  \_\_\_\_\_  $t =$  \_\_\_\_\_

(b) Re-write the first-order integrated rate law so that it is the form “ $y = mx + b$ ”

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(c) The following represents data from a first-order reaction. Fill in the missing data in the table. Then plot the data on the two graphs below.

Time (s)	[A] (M)	ln[A]
0	10.0	
10	7.94	
20	6.30	
30	5.00	
40	3.97	
50	3.15	
60	2.50	



(d) For a **first-order reaction**, which of the following will generate a straight-line graph?

[A] vs. time

ln[A] vs. time

1/[A] vs. time

(e) Calculate the slope of the straight line that was generated from the data in part (c). Include units in your answer.

(f) What does the value of this slope represent in the first-order rate law equation? \_\_\_\_\_

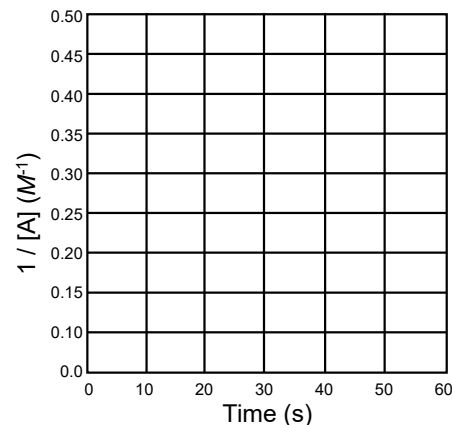
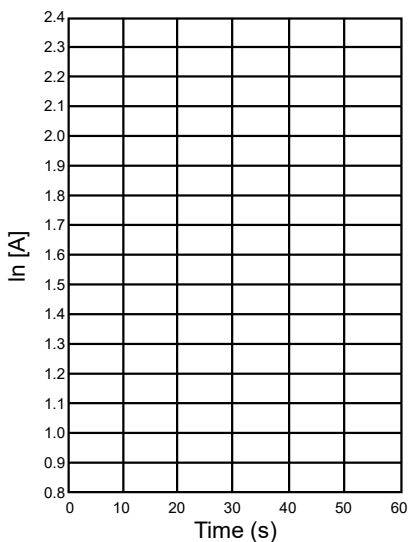
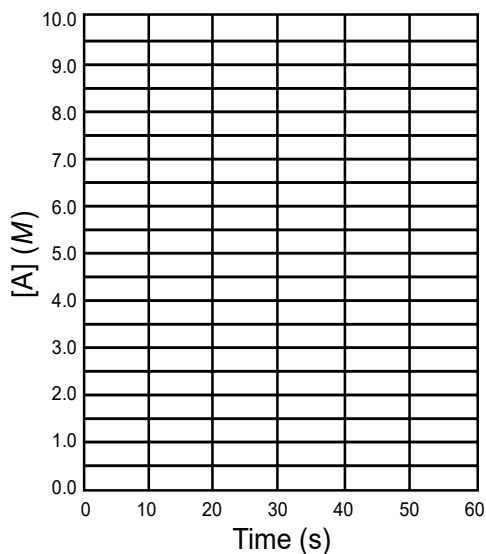
## II. Second Order Reactions

- For a second-order reaction, the rate law can be written as follows:  $\text{rate} = k [A]^2$
- From calculus, the following integrated rate law can be obtained:  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

(g) Re-write the second-order integrated rate law so that it is the form “ $y = mx + b$ ”

(h) The following represents data from a second-order reaction. Fill in the missing data in the table. Then plot the data on the three graphs below.

Time (s)	[A] (M)	ln[A]	1/[A] ( $M^{-1}$ )
0	10.0		
10	6.67		
20	5.00		
30	4.00		
40	3.33		
50	2.86		
60	2.50		



(i) For a *second-order reaction*, which of the following will generate a straight-line plot?

[A] vs. time

ln[A] vs. time

1/[A] vs. time

(j) Calculate the slope of the straight line that was generated from the data in part (h). Include units in your answer.

(k) What does the value of this slope represent in the second-order rate law equation? \_\_\_\_\_

### III. Zero Order Reactions

- For a zero-order reaction, the rate of the reaction (i.e., the disappearance of A) does NOT depend on the concentration of the reactant A.
- The rate law for a zero-order reaction can be written as follows: **rate = k**
- The following integrated rate law can be obtained:  $[A]_t - [A]_o = -kt$

(l) For a zero-order reaction, which of the following will generate a straight-line plot?

[A] vs. time

$\ln[A]$  vs. time

$1/[A]$  vs. time

### IV. Half Life

(m) Define the term **half-life** ( $t_{1/2}$ ).

(n) The following exercise will help you to understand the concept of half-life for a first-order reaction.

i. Write the integrated rate law for a first-order reaction:

ii. Substitute the following values for  $[A]_o$  and  $[A]_t$  into the equation:

$$[A]_o = 100 \quad [A]_t = 50$$

Simplify the equation and solve for t:

(o) Notice that **the half-life for a first-order rate law does NOT depend on the initial concentration of the reactant**. The half-life remains constant over time throughout the reaction.

i. Go back to the first-order data table in part (c).

How much time was required for the reactant concentration to change

from 10.0 M to 5.0 M? \_\_\_\_\_

ii. How much time was required for the reactant concentration to change

from 5.0 M to 2.5 M? \_\_\_\_\_

(p) You may recall that the rate constant for that first-order reaction in part (c) was equal to  $0.023 \text{ s}^{-1}$ . Verify that  $\frac{0.693}{k} = t_{1/2}$

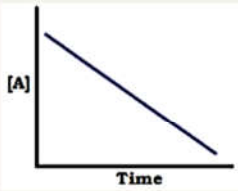
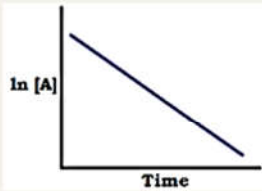

**If a decomposition reaction yields data that shows that the half-life is constant over time, then the reaction must be a first-order reaction.**

(q) The **half-life for a second-order reaction is NOT constant over time**. To verify this, go back to the second-order data table in part (h).

i. How much time was required for the reactant concentration to change from 10.0 M to 5.0 M? \_\_\_\_\_

ii. How much time was required for the reactant concentration to change from 5.0 M to 2.5 M? \_\_\_\_\_

### Summary:

	Zero Order	First Order	Second Order
<b>Rate Law</b>	Rate = k	Rate = k[A]	Rate = k[A] <sup>2</sup>
<b>Graph</b>			
<b>Linear fit</b>	[A] vs. time (negative)	ln [A] vs. time (negative)	1/[A] vs. time (positive)
<b>Integrated Rate Law</b>	$[A] = -k t + [A]_0$	$\ln [A] = -k t + \ln [A]_0$	$1/[A] = k t + 1/[A]_0$
<b>Rate Constant and Units</b>	Slope = -k, $\frac{\text{mol}}{\text{L} \cdot \text{sec}}$	Slope = -k, $\frac{1}{\text{sec}}$	Slope = k, $\frac{\text{L}}{\text{mol} \cdot \text{sec}}$
<b>Half Life Equation</b>	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k \cdot [A]_0}$
<b>Time for each half life</b>	Half as long for next half life	Same time for every half life	Double the time for next half life

**Example:**

Given the following reaction:  $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ , the concentration of  $\text{N}_2\text{O}_5$  was monitored over time.

Time (sec)	$[\text{N}_2\text{O}_5]$ (mol/L)	$\ln [\text{N}_2\text{O}_5]$	$1/[\text{N}_2\text{O}_5]$
0	0.100	-2.303	
50	0.0707	-2.649	
100	0.0500	-2.996	
200	0.0250	-3.689	
300	0.0125	-4.382	
400	0.00625	-5.075	

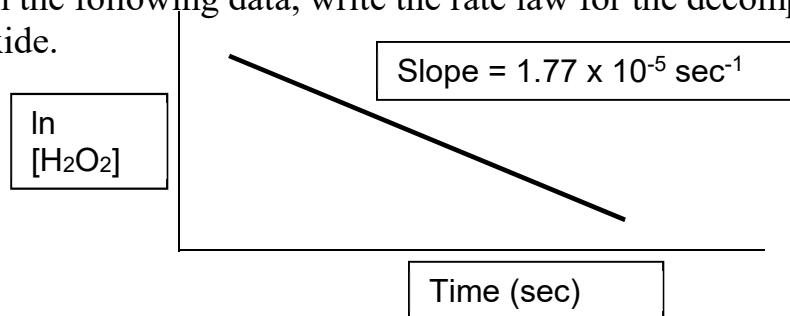
\*Note: sometimes you'll only be given the concentration data. If so, you can create a table on your graphing calculator to determine the values for  $\ln [x]$  and  $1/[X]$  and then create separate graphs to determine the reaction order.

- Determine the reaction order with respect to  $\text{N}_2\text{O}_5$ .
- Write the integrated rate law equation for this reaction.
- Determine the value of  $k$ , the rate law constant
- If the  $[\text{N}_2\text{O}_5]$  is initially 0.224 M, what is its concentration after 450 seconds?
- How long will it take the  $\text{N}_2\text{O}_5$  to decompose from 0.100 M to 0.0125 M?

### Integrated Rate Laws Problems

1. A first order reaction has a rate constant of  $1.00 \times 10^{-3} \text{ s}^{-1}$  and the initial concentration of the reactant is 1.50 M.
  - a. What is the concentration of the reactant at 1000. seconds?
  - b. Calculate the time that it would take for half of the initial concentration to be used.
2. A second order reaction has a rate constant of  $2.00 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  and the initial concentration of the reactant is 0.400 M.
  - a. What is the concentration of the reactant at 500. seconds?
  - b. How long would it take for the reactant to reach a concentration of 0.155 M?
3. A zero order has a rate constant of  $5.00 \times 10^{-4} \text{ M/s}$ . If the initial concentration of the reactant is 0.0800 M, at what time does the concentration reach 0.0300 M?

4. Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , decomposes into water and oxygen gas.
  - a. Given the following data, write the rate law for the decomposition of hydrogen peroxide.



- b. What is the rate constant for the decomposition of hydrogen peroxide in this experiment?
- c. What is the half-life of hydrogen peroxide in this experiment?

5. Using the information in the following table:

Time (seconds)	[B] (mol/L)
0.00	0.0100
1000	0.00625
1800	0.00476
2800	0.00370
3600	0.00313
4400	0.00270

a. Determine the order of reaction and write the general rate law.

b. Calculate the rate constant and provide correct units.

c. What is the concentration after 6500 seconds?

6. The following question refers to the gas-phase decomposition of ethylene chloride.



The experiment shows that the decomposition is first order. The following data shows kinetics information for this reaction:

<u>Time (sec)</u>	<u>ln [C<sub>2</sub>H<sub>5</sub>Cl] (M)</u>
1.0	-1.625
2.0	-1.735

a. What is the rate constant for this decomposition?

b. What was the initial concentration of the ethylene chloride?

c. What would the concentration be after 5.0 seconds?

d. What is its half-life?