5.1 Reaction Rates

Essential knowledge statements from the AP Chemistry CED:

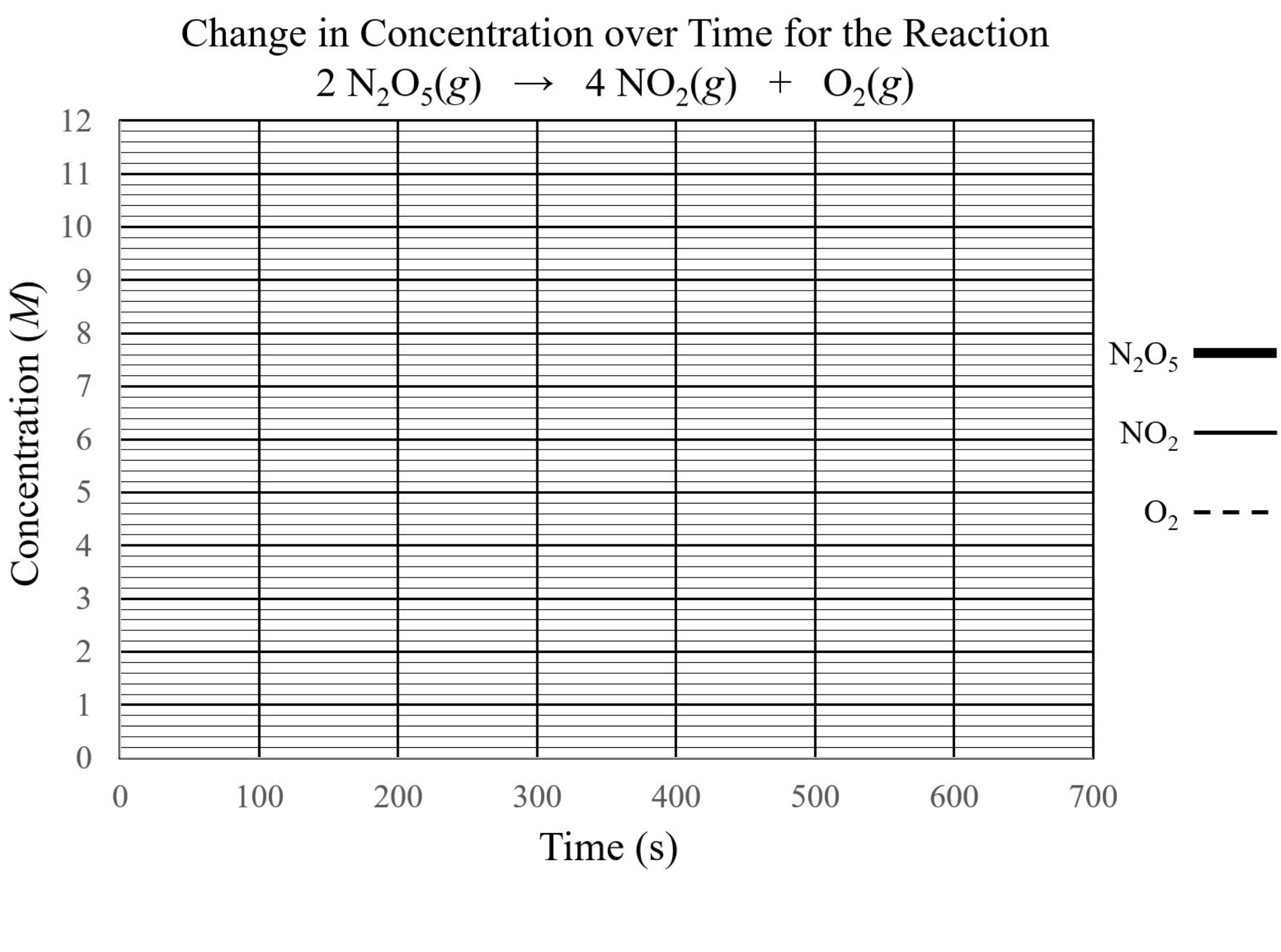
- The kinetics of a chemical reaction is defined as the rate at which an amount of reactants is converted to products per unit of time.
- The rates of change of reactant and product concentrations are determined by the stoichiometry in the balanced chemical equation.
- The rate of a reaction is influenced by reactant concentrations, temperature, surface area, catalysts, and other environmental factors.

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

An experiment is performed in which a sample of $N_2O_5(g)$ is added to a previously evacuated flask. A decomposition reaction occurs according to the chemical equation shown above. The table below represents data from the experiment as the reaction proceeds over time.

Time (s)	0	100	200	300	400	500	600	700
Concentration of N_2O_5 (*M*)	5.70	4.30	3.10	2.10	1.30	0.70	0.30	0.10
Concentration of NO_2 (*M*)	0	2.80	5.20	7.20	8.80	10.0	10.8	11.2
Concentration of O_2 (*M*)	0	0.70	1.30	1.80	2.20	2.50	2.70	2.80

1. Plot the data from the table on the graph below. Draw a smooth line to connect the data points for each substance. Use a thick solid line for $N_2O_5(g)$, a thin solid line for $NO_2(g)$, and a dashed line for $O_2(g)$.



$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

2. Consider the reaction between $NH_3(g)$ and $O_2(g)$ that is represented by the equation shown above.

   At a certain point in time during the reaction, the rate of disappearance of $NH_3(g)$ was equal to $0.64\ M\ s^{-1}$.

   (a) Calculate the rate of disappearance of $O_2(g)$ at that same point in time. Include units in your answer.

   (b) Calculate the rate of appearance of $H_2O(g)$ at that same point in time. Include units in your answer.

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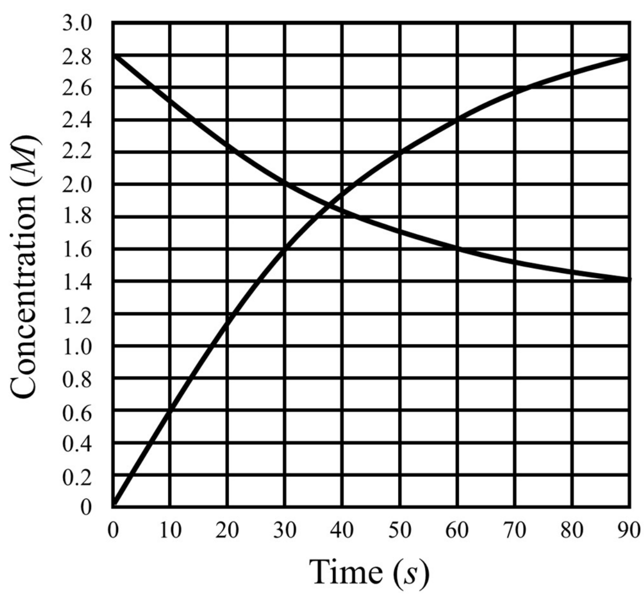
3. The diagram below represents the data from an experiment in which the concentrations of both reactants and products are measured over time during the reaction.



   (a) Label each curve in the diagram above as "reactants" or "products." Justify your answer.

   (b) Which of the following chemical equations is most likely to represent the reaction that occurred during this experiment? Justify your answer.

$XYZ \rightarrow XZY$ $\qquad\qquad$ $2\ X \rightarrow X_2$ $\qquad\qquad$ $X_2 \rightarrow 2\ X$

According to **collision theory**, which will be discussed in Topic 5.5, reactant particles must undergo successful collisions in order for products to be formed in a chemical reaction.

$$Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

4. A series of experiments is performed by combining Mg(*s*) with HCl(*aq*). The reaction occurs according to the equation shown above. The initial reaction rate is determined from the experimental data for each trial.

Trial	Mass of Mg(*s*)	Form of Mg(*s*)	Volume of HCl(*aq*)	Concentration of HCl(*aq*)	Temperature of HCl(*aq*)
1	5.0 g	metal strip	100 mL	2.0 *M*	20°C
2	5.0 g	metal strip	100 mL	4.0 *M*	20°C
3	5.0 g	metal strip	100 mL	2.0 *M*	40°C
4	5.0 g	metal powder	100 mL	2.0 *M*	20°C

For each of the following, give an explanation than describes how the collisions between reactant particles are affected by the experimental conditions.

(a) Explain why the initial reaction rate in Trial 2 is faster than the initial rate in Trial 1.

(b) Explain why the initial reaction rate in Trial 3 is faster than the initial rate in Trial 1.

(c) Explain why the initial reaction rate in Trial 4 is faster than the initial rate in Trial 1.

5. At what point in time during a chemical reaction should the reaction rate have the greatest value? Justify your answer based on the relationship between concentration and rate.

In addition to the variables of concentration, temperature, and surface area, another factor that can affect the reaction rate is the presence of a catalyst. Catalysis will be discussed in Topic 5.11.

5.2 Introduction to Rate Law

Essential knowledge statements from the AP Chemistry CED:

- Experimental methods can be used to monitor the amounts of reactants and/or products of a reaction and to determine the rate of the reaction.
- The rate law expresses the rate of a reaction as proportional to the concentration of each reactant raised to a power.
- The power of each reactant in the rate law is the order of the reaction with respect to that reactant. The sum of the powers of the reactant concentrations in the rate law is the overall order of the reaction.
- The proportionality constant in the rate law is called the rate constant. The value of this constant is temperature dependent and the units reflect the overall reaction order.
- Comparing initial rates of a reaction is a method to determine the order with respect to each reactant.

One way to study the rate of a chemical reaction is to investigate how changes in the initial concentration of the reactants will affect the initial reaction rate.

$$2\ NO(g) \ +\ 2\ H_2(g) \ \rightarrow\ N_2(g) \ +\ 2\ H_2O(g)$$

6. An experiment is performed to study the kinetics of the reaction between $NO(g)$ and $H_2(g)$, as represented by the equation above. The data from the experiment is summarized in the table below.

Experiment	Initial [NO] (M)	Initial [H_2] (M)	Initial Rate of Formation of N_2 (M/s)
Trial 1	0.10	0.10	1.2×10^{-3}
Trial 2	0.10	0.20	2.4×10^{-3}
Trial 3	0.20	0.10	4.8×10^{-3}
Trial 4	0.20	0.20	?

Note: When you see a chemical formula surrounded by brackets [ ], this notation refers to the concentration of that substance, in units of moles per liter.

(a) Compare the data from Trials 1 and 2. The initial concentration of H_2 is ___________________ while the initial concentration of NO remains constant. As a result of this change, the initial rate of formation of N_2 is ___________________. Therefore we can say that this reaction is *first order with respect to H_2.*

(b) Compare the data from Trials 1 and 3. The initial concentration of NO is ___________________ while the initial concentration of H_2 remains constant. As a result of this change, the initial rate of formation of N_2 is ___________________. Therefore we can say that this reaction is *second order with respect to NO.*

Now that we know the order with respect to each reactant, we can write the rate law.

$$\text{rate} = k[NO]^2[H_2]$$

7. Use the rate law shown above and the information in the data table on the previous page to answer the following questions.

   (a) Calculate the value of the rate constant k for this reaction. Include units in your answer.

   (b) Calculate the initial rate of formation of N_2 in Trial 4. Include units in your answer.

The following statements provide important information about rate laws and the process of determining the order with respect to a certain reactant in a chemical reaction.

- The order with respect to a certain reactant is a numerical value that…
  - …is usually a number equal to zero, one, or two.
  - …is determined from experimental data.
  - …indicates how the change in the initial concentration of that reactant will affect the initial reaction rate.
- The order with respect to a certain reactant may, in fact, be the same as the coefficient of that reactant in the overall balanced chemical equation. However, this is not always true. That is why the order with respect to a certain reactant must be determined from experimental data.
- The value of the rate constant (k) can be calculated from experimental data. The value of k is unique for a particular chemical reaction, and is dependent on the temperature at which the reaction is carried out.
- If you change the initial temperature at which the reaction is performed, the value of the rate constant (k) will also change.
- If you only change the initial concentration(s) of the reactant(s) while keeping the initial temperature constant, the value of the rate constant (k) will remain the same.

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

8. Experimental data indicates that the reaction represented by the equation above is first order with respect to N_2O_5.Write the rate law for this reaction.

9. The overall reaction order is the sum of the orders with respect to each reactant in the rate law. The units of the rate constant (k) depend on the overall reaction order. For each rate law in the table below, assume that the units of the rate are M/s. Fill in the missing information in the table below.

Rate Law	Overall reaction order	Units of the rate constant k
rate = k		
rate = k [A]		
rate = k $[A]^2$		
rate = k [A][B]		
rate = k $[A]^2[B]$		

A (reactant) $\rightarrow$ B (product)

10. Answer the following questions related to the rate law for a generic reaction (A → B), in which the identity of the reactant is represented by the letter "A."

(a) Suppose that a reaction is **zero order** with respect to A.

If the initial value of [A] is doubled, the initial reaction rate will ________________________

(b) Suppose that a reaction is **first order** with respect to A.

If the initial value of [A] is doubled, the initial reaction rate will ________________________

(c) Suppose that a reaction is **second order** with respect to A.

If the initial value of [A] is doubled, the initial reaction rate will ________________________

$$2\,ClO_2(aq) + 2\,OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O(l)$$

11. A student studies the kinetics of the reaction between ClO_2 and OH^-, as represented by the equation above. Data from the experiment is shown in the following table.

Experiment	Initial $[ClO_2]$ (M)	Initial $[OH^-]$ (M)	Initial Rate of Appearance of ClO_2^- (M/s)
Trial 1	0.060	0.030	0.0248
Trial 2	0.020	0.030	0.00276
Trial 3	0.020	0.090	0.00828
Trial 4	0.050	0.050	?

(a) Determine the order of the reaction with respect to ClO_2. Justify your answer.

(b) Determine the order of the reaction with respect to OH^-. Justify your answer.

(c) Write the rate law for the reaction. ______________________________

(d) Calculate the value of the rate constant k for this reaction. Include units in your answer.

(e) Calculate the initial rate of appearance of ClO_2^- in Trial 4. Include units in your answer.

5.3 Concentration Changes Over Time

Essential knowledge statements from the AP Chemistry CED:

- The order of a reaction can be inferred from a graph of concentration of reactant versus time.
- If a reaction is first order with respect to a reactant being monitored, a plot of the natural log (ln) of the reactant concentration as a function of time will be linear.
- If a reaction is second order with respect to a reactant being monitored, a plot of the reciprocal of the concentration of that reactant versus time will be linear.
- The slopes of the concentration versus time data for zeroth, first, and second order reactions can be used to determine the rate constant for the reaction.
  - Zeroth-order equation: $[A]_t - [A]_0 = -kt$
  - First-order equation: $\ln[A]_t - \ln[A]_0 = -kt$
  - Second-order equation: $1/[A]_t - 1/[A]_0 = kt$
- Half-life is a critical parameter for first order reactions because the half-life is constant and related to the rate constant for the reaction by the following equation: $t_{½} = 0.693/k$
- Radioactive decay processes provide an important illustration of first order kinetics.

$$\text{A (reactant)} \rightarrow \text{B (product)}$$

Consider a generic reaction (A → B), in which the identity of the reactant is represented by the letter "A." Suppose that it has been determined from the analysis of experimental data that the reaction is first order with respect to A. The rate law would be written as follows.

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

We can use calculus to transform this rate law into the following expression.

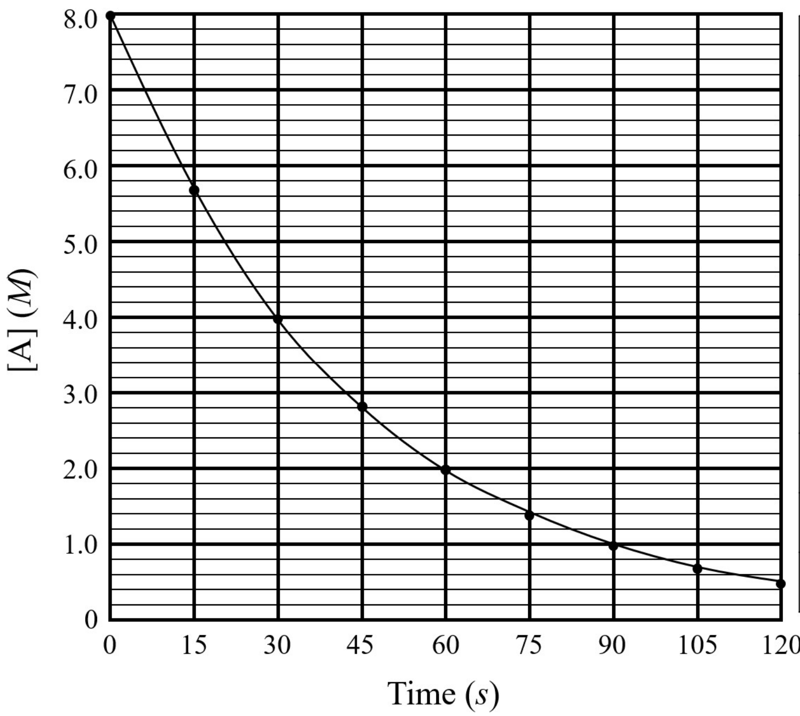
$$\ln[A]_t - \ln[A]_0 = -kt$$

This equation is the **first-order integrated rate law equation**.

k = the rate constant, t = time

$[A]_0$ = the initial concentration of A at time = zero

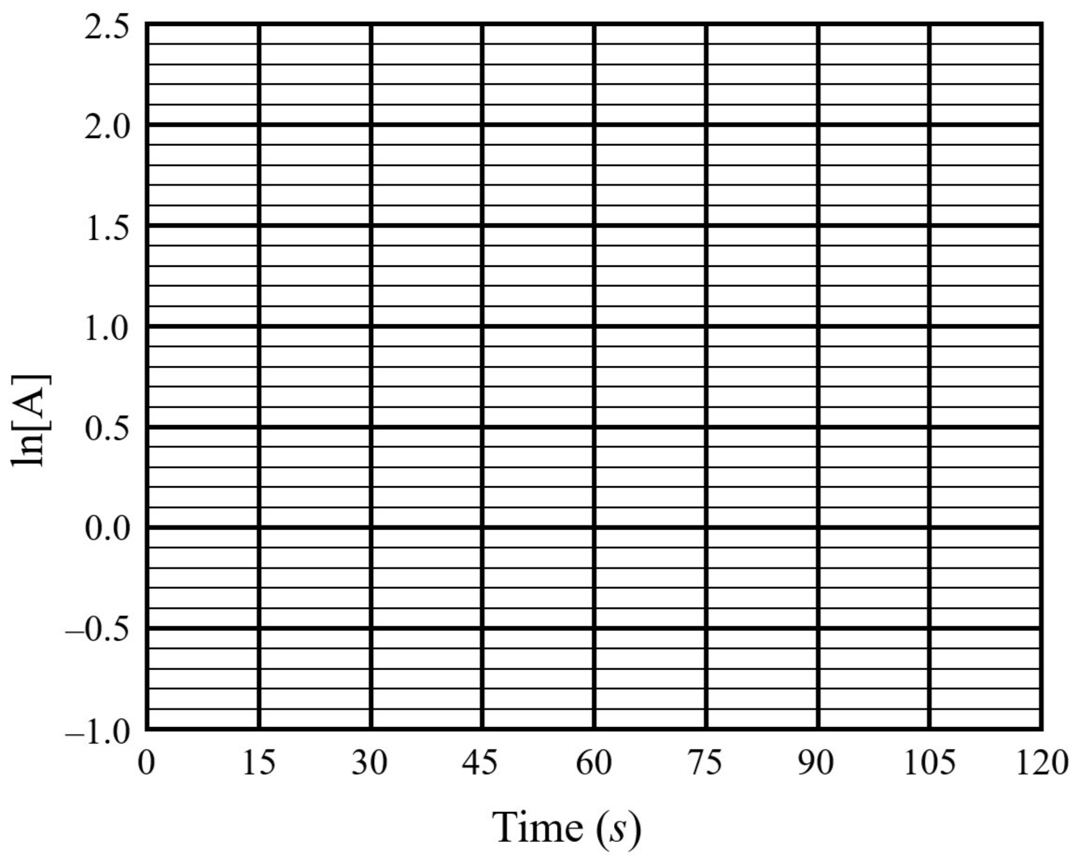
$[A]_t$ = the concentration of A at some point in time, equal to t



Time (*s*)	[A] (*M*)	ln[A]
0	8.00	
15	5.66	
30	4.00	
45	2.83	
60	2.00	
75	1.41	
90	1.00	
105	0.71	
120	0.50	

12. (a) Use the data for [A] in the table above to calculate the value of ln[A]. Record the calculated values of ln[A] in the data table.

(b) Plot the data for ln[A] versus time on the graph below.



If a reaction is first order with respect to A, then the plot of ln[A] versus time will be a straight line. The absolute value of the slope of this line is equal to value of the rate constant (*k*).

12. (c) Draw a straight line through the data points on the graph that you created in part (b). Calculate the value of the slope of this line, and include units in your answer. ______________________________

    Note that [A] has units of *M* or mol/L, but the quantity "ln[A]" has no units.

The **half-life ($t_{½}$)** of a reaction is defined as the time required for the concentration of a reactant to reach half of its original value.

If a reaction is first order with respect to a particular reactant, then the half-life of that reactant should remain constant over time during the course of the reaction.

The converse of this statement is also true.

If the half-life of a particular reactant remains constant over time during course of the reaction, then the reaction should be first order with respect to that reactant.

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12. (d) Based on the data for [A] versus time shown on the previous page, determine the half-life of reactant A. Include units in your answer. ___________________________________

Here is a portion of the AP Chemistry Equations and Constants Sheet. I have added labels for the equations that refer to zeroth-order, first-order, and second-order kinetics.

KINETICS

$$[A]_t - [A]_0 = -kt$$ → **zeroth-order equation**

$$\ln[A]_t - \ln[A]_0 = -kt$$ → **first-order equation**

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$ → **second-order equation**

$$t_{½} = \frac{0.693}{k}$$ → **first-order equation**

k = rate constant
t = time
$t_{½}$ = half-life

12. (e) Use your answer to part (d) and the half-life equation $t_{½} = 0.693/k$ to calculate the value of the rate constant (k). Include units in your answer. _______________________________________

Suppose that it has been determined from the analysis of experimental data that a reaction is second order with respect to reactant A. The rate law would be written as follows.

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

We can use calculus to transform this rate law into the following expression.

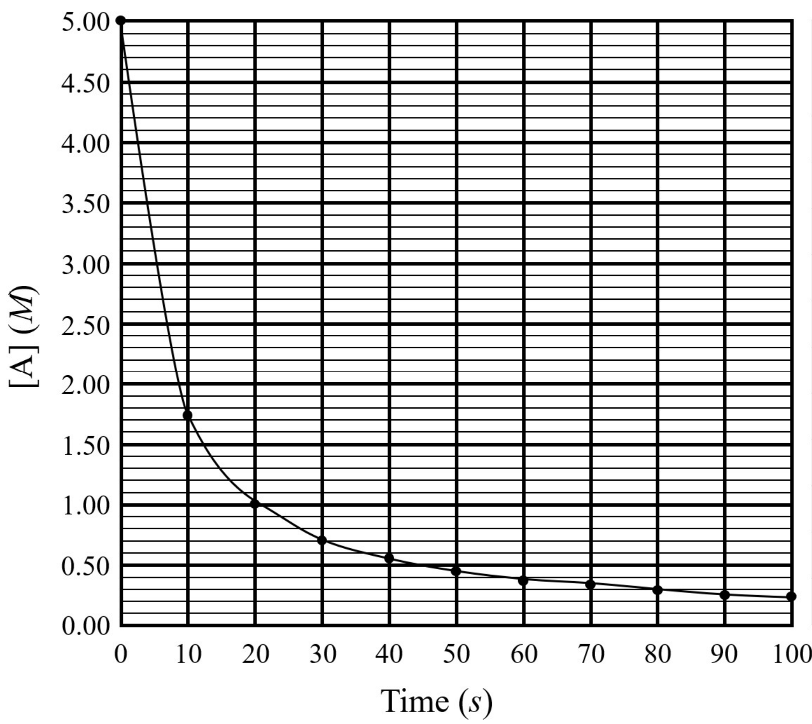
$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

This equation is the **second-order integrated rate law equation**.

k = the rate constant, t = time

$[\mathrm{A}]_0$ = the initial concentration of A at time = zero

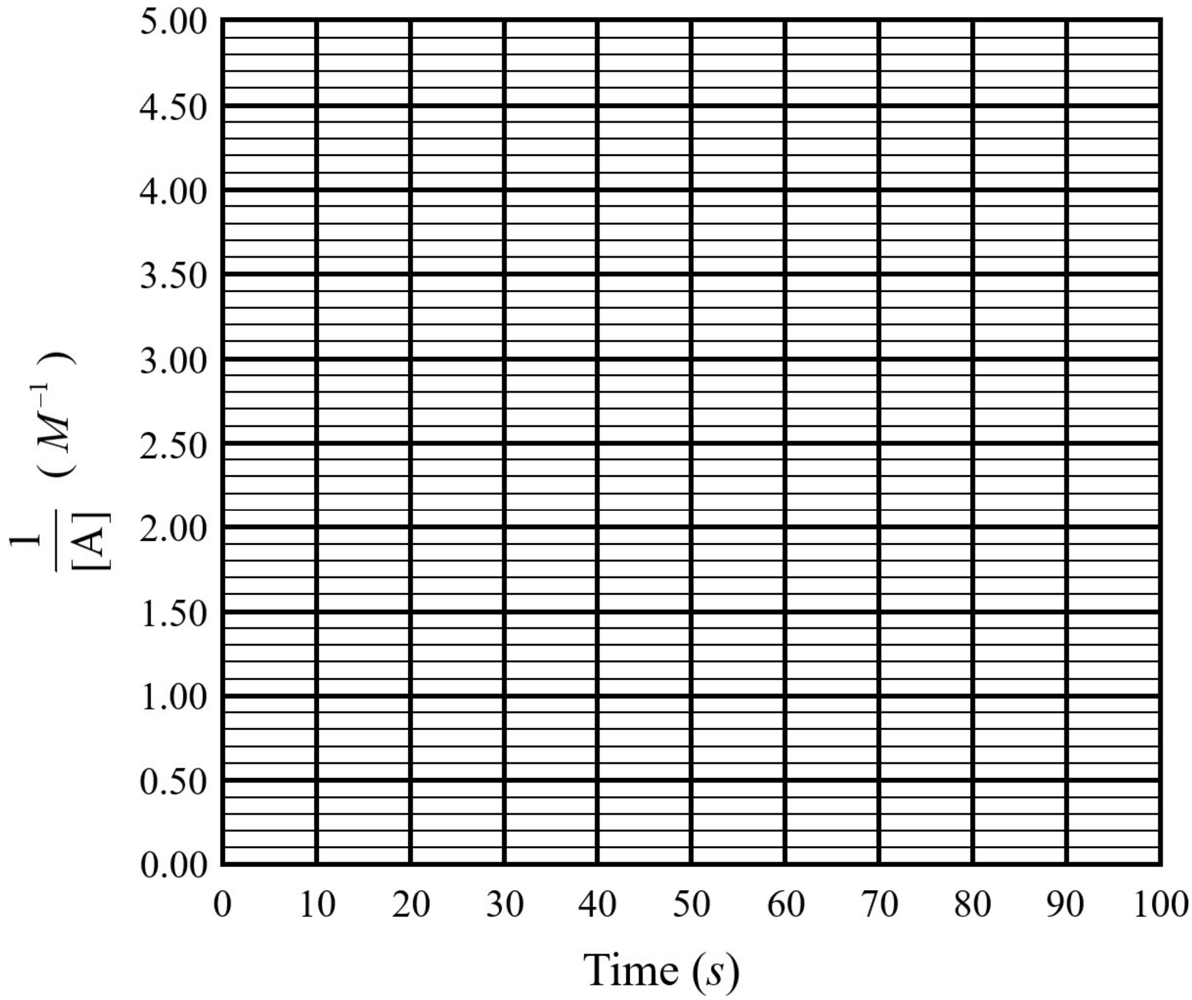
$[\mathrm{A}]_t$ = the concentration of A at some point in time, equal to t



Time (*s*)	[A] (*M*)	$\frac{1}{[\mathrm{A}]}$ (M^{-1})
0	5.00	
10	1.67	
20	1.00	
30	0.71	
40	0.56	
50	0.46	
60	0.38	
70	0.33	
80	0.29	
90	0.26	
100	0.24	

13. (a) Use the data for [A] in the table above to calculate the value of 1/[A]. Record the calculated values of 1/[A] in the data table.

13. (b) Plot the data for 1/[A] versus time on the graph below.



If a reaction is second order with respect to A, then the plot of 1/[A] versus time will be a straight line. The absolute value of the slope of this line is equal to value of the rate constant (*k*).

13. (c) Draw a straight line through the data points on the graph that you created in part (b). Calculate the value of the slope of this line, and include units in your answer. ______________________________

Suppose that it has been determined from the analysis of experimental data that a reaction is zeroth order with respect to reactant A. The rate law would be written as follows.

$$\text{rate} = k$$

We can use calculus to transform this rate law into the following expression.

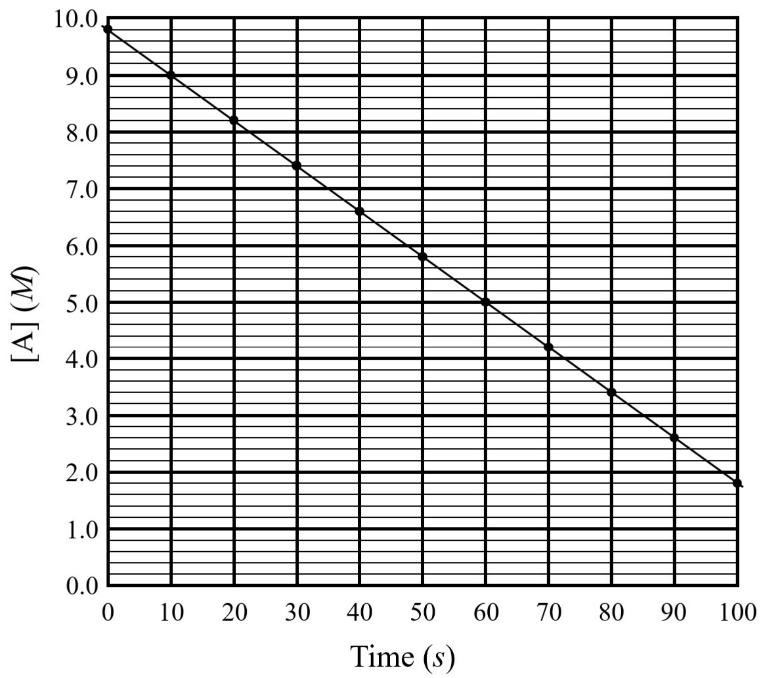
$$[A]_t - [A]_0 = -kt$$

This equation is the **zeroth-order integrated rate law equation**.

k = the rate constant, t = time

$[A]_0$ = the initial concentration of A at time = zero

$[A]_t$ = the concentration of A at some point in time, equal to t



Time (s)	[A] (M)
0	9.8
10	9.0
20	8.2
30	7.4
40	6.6
50	5.8
60	5.0
70	4.2
80	3.4
90	2.6
100	1.8

If a reaction is zeroth order with respect to A, then the plot of [A] versus time will be a straight line. The absolute value of the slope of this line is equal to value of the rate constant (*k*).

14. Calculate the value of the slope of the line shown in the diagram above. Include units in your answer. ______________________________________

15. Below is a summary of the information that has been presented so far. Fill in the missing information.

Order with Respect to A	Zero	First	Second
What does a graph of [A] versus time look like? (curve or straight line)			
Does the half-life of A remain constant over time?			
What type of graph should produce a straight line?			
How do you determine the value of *k* from the linear graph mentioned above?			
Suppose that the reaction rate has units of *M*/s. What are the units of the rate constant (*k*)?			

Radioactive decay processes provide an important illustration of first order kinetics. In nuclear decay, the composition of the atomic nucleus changes. In a chemical reaction, chemical bonds are broken and/or formed. Since the half-life remains constant during nuclear decay, it is classified as a first order process.

16. Nitrogen-13 (^{13}N) is an isotope of nitrogen that undergoes a nuclear decay process in which it is converted into carbon-13 (^{13}C). The half-life for this decay process is equal to 10 minutes.

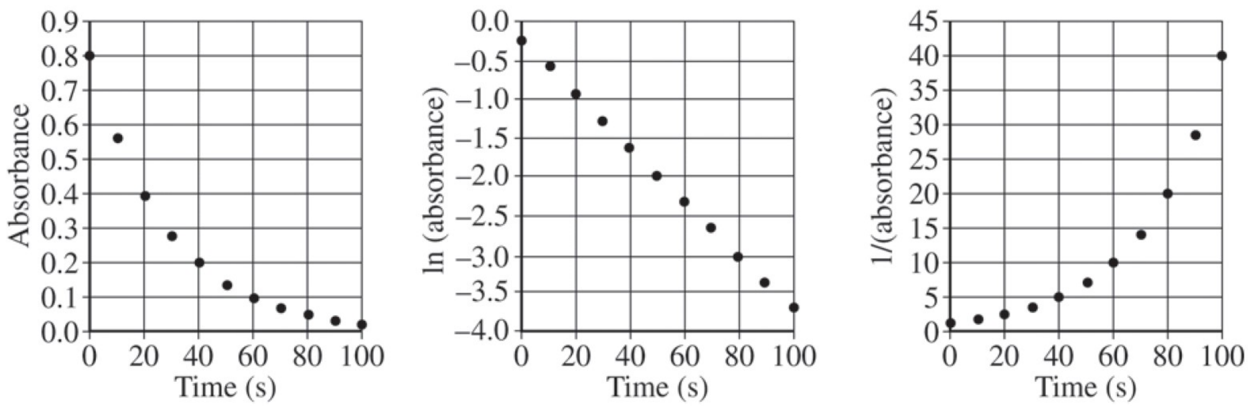
    (a) Calculate the value of the rate constant (*k*) for the radioactive decay of ^{13}N. Include units in your answer. ____________________________

    (b) Suppose that you have a pure sample of ^{13}N that has a mass of 64 mg. Calculate the mass, in units of mg, of ^{13}N that will be present in this sample after a period of 50 minutes.

    (c) Suppose that you have a pure sample of ^{13}N that has a mass of 125 mg. Calculate the mass, in units of mg, of ^{13}N that will be present in this sample after a period of 37 minutes.

$$\underset{\text{(blue food coloring)}}{Na_2C_{37}H_{34}N_2S_3O_9(aq)} + \underset{\text{(bleach)}}{NaOCl(aq)} \rightarrow \underset{\text{(colorless)}}{\text{products}}$$

17. Blue food coloring ($Na_2C_{37}H_{34}N_2S_3O_9$) reacts with household bleach ($NaOCl$) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the blue food coloring over time during the course of the reaction. The experiment is run with an initial concentration of bleach that is much greater than the initial concentration of blue food coloring. This ensures that the concentration of bleach remains essentially constant throughout the reaction. The student used the data from the experiment to generate the graphs shown below.



Graph I Graph II Graph III

(a) What is the order of the reaction with respect to the blue food coloring? Justify your answer.

(b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance value of zero too rapidly. In order to correct this problem, the student proposes the following three possible modifications to the experiment.

increasing the temperature	increasing the concentration of the blue food coloring	increasing the concentration of the bleach

Which of these proposed modifications should correct the problem? Explain how that modification increases the time required for the reaction mixture to reach an absorbance value of zero.

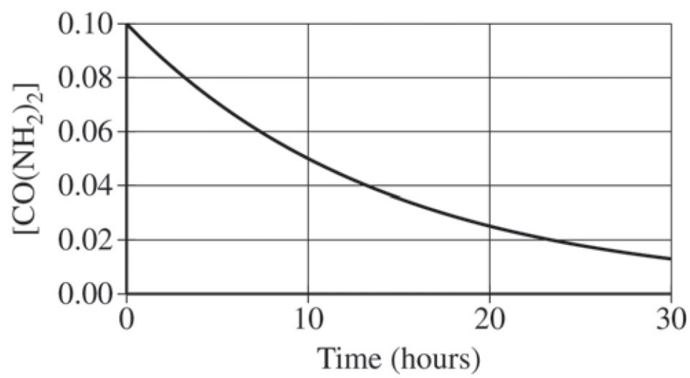
17. (continued)

(c) In another experiment, a student wishes to study the reaction between red food coloring and bleach. Describe how the student should modify the original experimental procedure in order to determine the order of the reaction with respect to the red food coloring.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

18. A student studying the decomposition of $CO(NH_2)_2$ represented by the equation shown above runs the reaction at 90°C. The student collects data on the concentration of $CO(NH_2)_2$ as a function of time, as shown by the data table and the graph below.

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



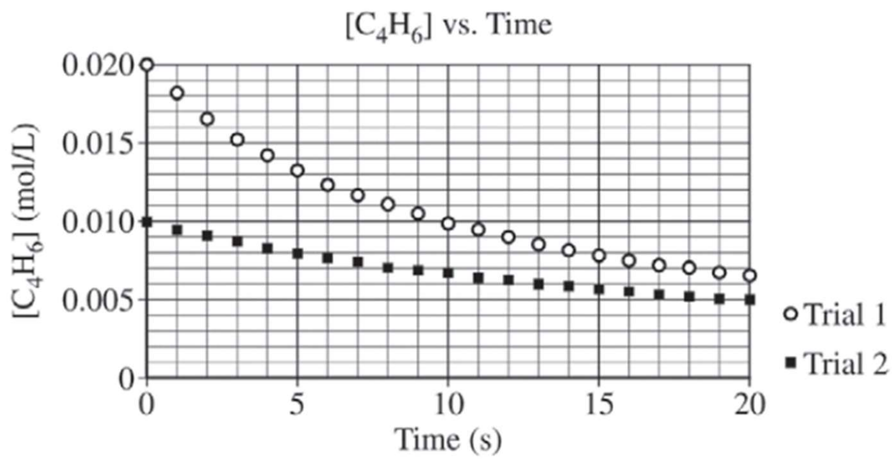
(a) What is the order of the reaction with respect to $CO(NH_2)_2$? Justify your answer.

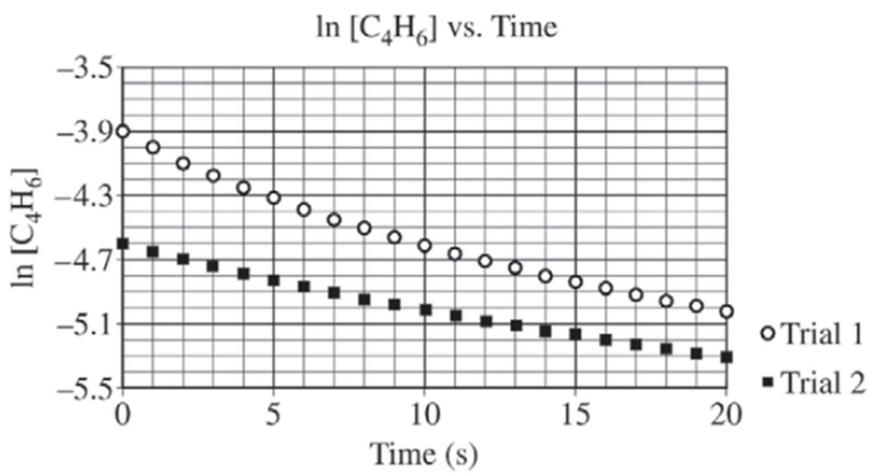
(b) Determine the value of the rate constant k for this decomposition reaction at 90°C. Include units with your answer.

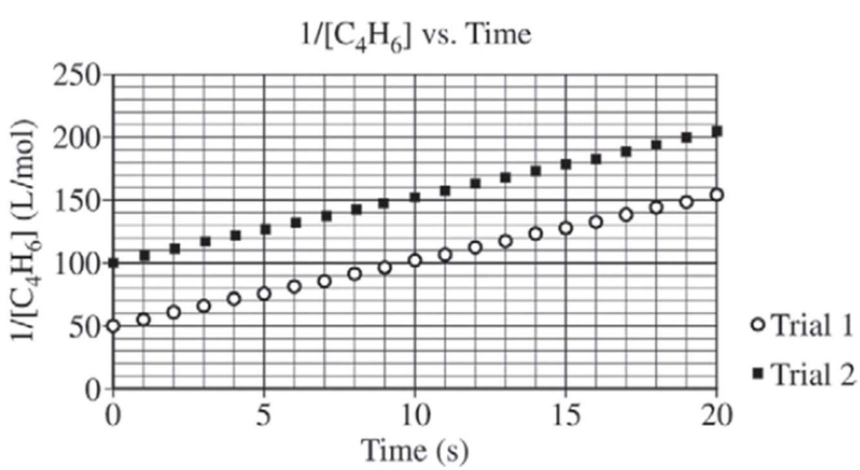
(c) Calculate the expected value for the concentration of $CO(NH_2)_2$ in this experiment after 35 hours have passed.

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

19. At high temperatures, the compound C_4H_6 reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.







19. (continued)

(a) For Trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

(b) What is the order of the reaction with respect to C_4H_6? Justify your answer.

(c) The initial rate of the reaction in trial 1 is equal to 0.0010 $M\ s^{-1}$. Calculate the value of the rate constant, k, for the reaction at 625 K. Include units in your answer.

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

20. The decomposition of $H_2O_2(aq)$ is represented by the equation above. A student monitored the decomposition of a sample of $H_2O_2(aq)$ at a constant temperature and recorded the concentration of H_2O_2 as a function of time. The results are given in the table below.

Time (*h*)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$	$1/[H_2O_2]$ (M^{-1})
0	1.000		
2	0.794		
4	0.630		
6	0.500		

(a) Calculate the missing values in the table above.

(b) Determine the order of the reaction with respect to H_2O_2. Justify your answer.

(c) Determine the value of the rate constant k for this decomposition reaction. Include units with your answer. ______________________________

(d) Determine the half-life of H_2O_2 in this experiment. Include units in your answer. ____

(e) Calculate the expected value for the concentration of H_2O_2 in this experiment after 8 hours have passed.