

AP Chemistry Unit 5 Easier Practice Set

Chemical Kinetics

Building Confidence with Reaction Rates & Mechanisms

APChemistryRescue.com



Practice Set Information

- **Total Points:** 75 points
- **Suggested Time:** 70–100 minutes
- **Questions:** 10 (scaffolded from rate calculations → rate laws → mechanisms → Arrhenius)
- **Topics:** Reaction rates, rate laws, integrated rate laws, reaction mechanisms, activation energy, catalysis
- **Skills:** Initial rate method, graphing $\ln[A]$ and $1/[A]$, energy diagrams, mechanism analysis, Arrhenius calculations



ESSENTIAL KINETICS FORMULAS

RATE EXPRESSIONS :

$$\text{Rate} = k[A]^m[B]^n \text{ (rate law)}$$

$$\text{Rate} = -\Delta[A]/\Delta t \text{ (for reactant A)}$$

$$\text{Rate} = \Delta[P]/\Delta t \text{ (for product P)}$$

INTEGRATED RATE LAWS :

$$\text{Zero-order: } [A]_t = -kt + [A]_0$$

$$\text{First-order: } \ln[A]_t = -kt + \ln[A]_0$$

$$\text{Second-order: } 1/[A]_t = kt + 1/[A]_0$$

HALF-LIFE FORMULAS:

First-order: $t_{1/2} = 0.693/k$ (independent of $[A]_0$)

Zero-order: $t_{1/2} = [A]_0 / (2k)$

Second-order: $t_{1/2} = 1 / (k[A]_0)$

ARRHENIUS EQUATION:

$$k = Ae^{-Ea/RT}$$

$$\ln k = -\frac{Ea}{R} \left(\frac{1}{T}\right) + \ln A$$

$$R = 8.314 \text{ J/(mol}\cdot\text{K)}$$



Kinetics Success Tips:

- **Rate law orders are determined EXPERIMENTALLY**
—NOT from the balanced equation (unless it's an elementary step)
- **To find reaction order:**
Use initial rate method—double [A] and see if rate doubles (1st order), quadruples (2nd order), or stays same (0th order)
- **For graphing:**
Zero-order \rightarrow plot $[A]$ vs. t (linear); First-order $\rightarrow \ln[A]$ vs. t (linear); Second-order $\rightarrow 1/[A]$ vs. t (linear)
- **Mechanism rules:**
(1) Steps add to overall equation; (2) Rate law comes from slowest (RDS) step; (3) Intermediates cancel out
- **Energy diagrams:**
Catalysts lower E_a but do NOT change ΔH ; transition state is at the peak, NOT a valley

Question 1: Calculating Average Rate (6 points)

The decomposition of ozone (O_3) in the atmosphere follows the reaction:



The concentration of O_3 decreases from 0.040 M to 0.028 M over a time interval of 12.0 seconds.

(a) Calculate the **average rate of disappearance** of O_3 over this time interval. Use $\text{Rate} = -\Delta[\text{O}_3]/\Delta t$. Show all work with units.

Work Space:

(b) Calculate the **average rate of formation** of O_2 over this time interval. (Hint: Use the stoichiometric ratio 2:3 from the balanced equation.)

Stoichiometric Relationship:

$$\text{Rate of } \text{O}_2 \text{ formation} = (3/2) \times \text{Rate of } \text{O}_3 \text{ disappearance}$$

Work Space:

Question 2: Initial Rate Method to Determine Order (10 points)

The reaction between substances A and B is studied:



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

The following initial rate data are collected:

Experiment	[A] ₀ (M)	[B] ₀ (M)	Initial Rate (M/s)
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	8.0×10^{-3}
3	0.10	0.20	4.0×10^{-3}

(a) Determine the **order with respect to A** (value of m). Compare Experiments 1 and 2 (where [B] is constant).

Method:

- [A] changes from 0.10 to 0.20 (doubles)
- Rate changes from 2.0×10^{-3} to 8.0×10^{-3} (quadruples = $2^2 = 4$)
- Therefore: rate $\propto [A]^2$, so m = 2

Work Space:

(b) Determine the **order with respect to B** (value of n). Compare Experiments 1 and 3 (where [A] is constant).

Work Space:

(c) Write the **complete rate law** for this reaction, including the values of m and n.

Work Space:

(d) Calculate the **rate constant k** using data from Experiment 1. Include proper units.

Work Space:

(e) What is the **overall reaction order**? (Sum of m + n.)

Work Space:

Question 3: First-Order Kinetics and Half-Life (8 points)

The radioactive decay of carbon-14 is a first-order process with a rate constant $k = 1.21 \times 10^{-4} \text{ yr}^{-1}$.



(a) Calculate the **half-life** of ^{14}C using $t_{1/2} = 0.693/k$. Show all work with units.

Work Space:

(b) If a sample initially contains 100.0 g of ^{14}C , how much will remain after **5730 years** (one half-life)?

Work Space:

(c) How much ^{14}C will remain after **11,460 years** (two half-lives)?

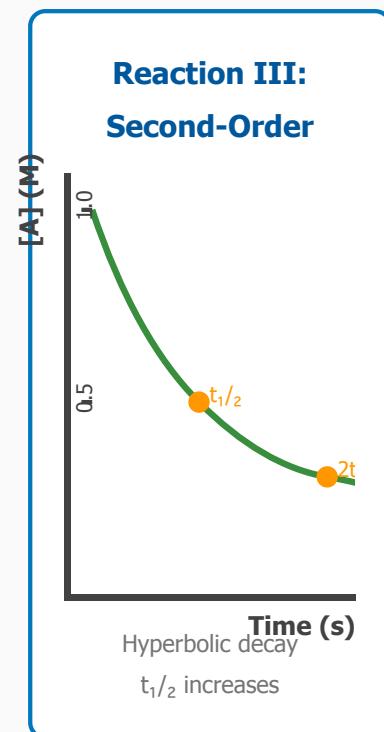
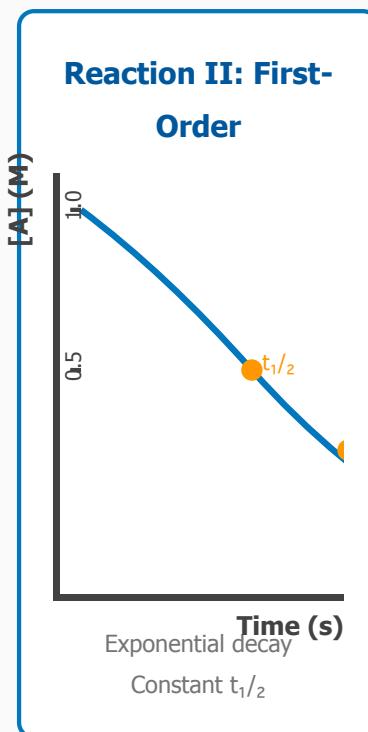
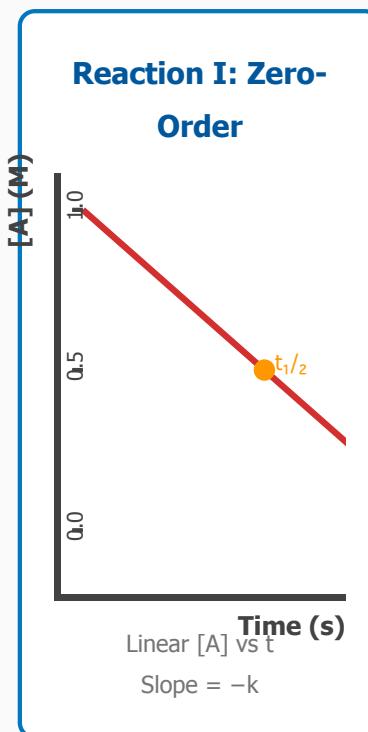
Work Space:

(d) Explain why the half-life of a **first-order reaction** is **independent** of the initial concentration $[A]_0$. (Contrast with zero-order or second-order.)

Work Space:

Question 4: Concentration vs. Time Graphs (8 points)

Three reactions (Reaction I, II, and III) have different rate laws. The concentration of reactant A vs. time is plotted for each:



(a) For **Reaction I (zero-order)**, the graph shows a **linear** relationship between $[A]$ and time. Write the equation of this line and identify what the slope represents.

Work Space:

(b) For **Reaction II (first-order)**, why is the half-life **constant** (equal time intervals for $[A]$ to halve)?

Work Space:

(c) For **Reaction III (second-order)**, why does the half-life **increase** as the reaction progresses (compare $t_{1/2}$ to $2t_{1/2}$ intervals)?

Work Space:

(d) If you wanted to verify that Reaction II is truly first-order, what should you plot on the y-axis vs. time on the x-axis to obtain a straight line?

Work Space:

Question 5: Integrated Rate Law and Graphing (9 points)

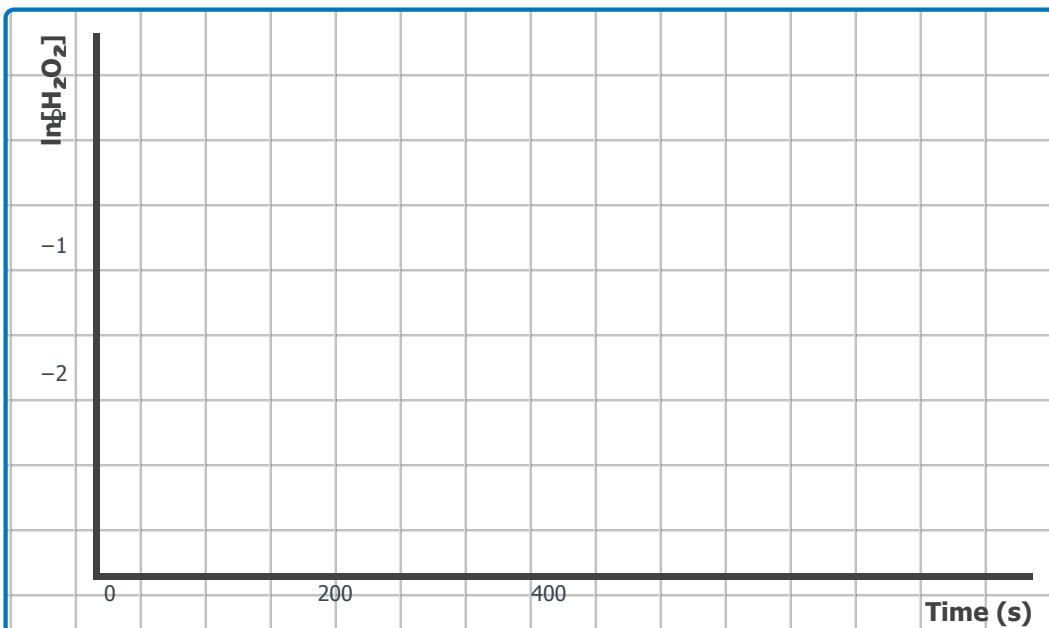
The decomposition of hydrogen peroxide is studied:



The following concentration-time data are collected:

Time (s)	$[\text{H}_2\text{O}_2]$ (M)	$\ln[\text{H}_2\text{O}_2]$	$1/[\text{H}_2\text{O}_2]$ (M ⁻¹)
0	1.00	0.00	1.00
100	0.61	-0.49	1.64
200	0.37	-0.99	2.70
300	0.23	-1.47	4.35
400	0.14	-1.97	7.14

(a) Plot $\ln[\text{H}_2\text{O}_2]$ vs. time on the grid below. If the plot is linear, the reaction is first-order.



Plot your points and draw a best-fit line.

(b) Is the plot of $\ln[H_2O_2]$ vs. time linear? What does this tell you about the reaction order?

Work Space:

(c) Calculate the **slope** of the $\ln[H_2O_2]$ vs. time line using two points (e.g., $t = 0$ and $t = 400$ s). The slope equals $-k$.

Slope formula:

$$m = (y_2 - y_1)/(x_2 - x_1)$$

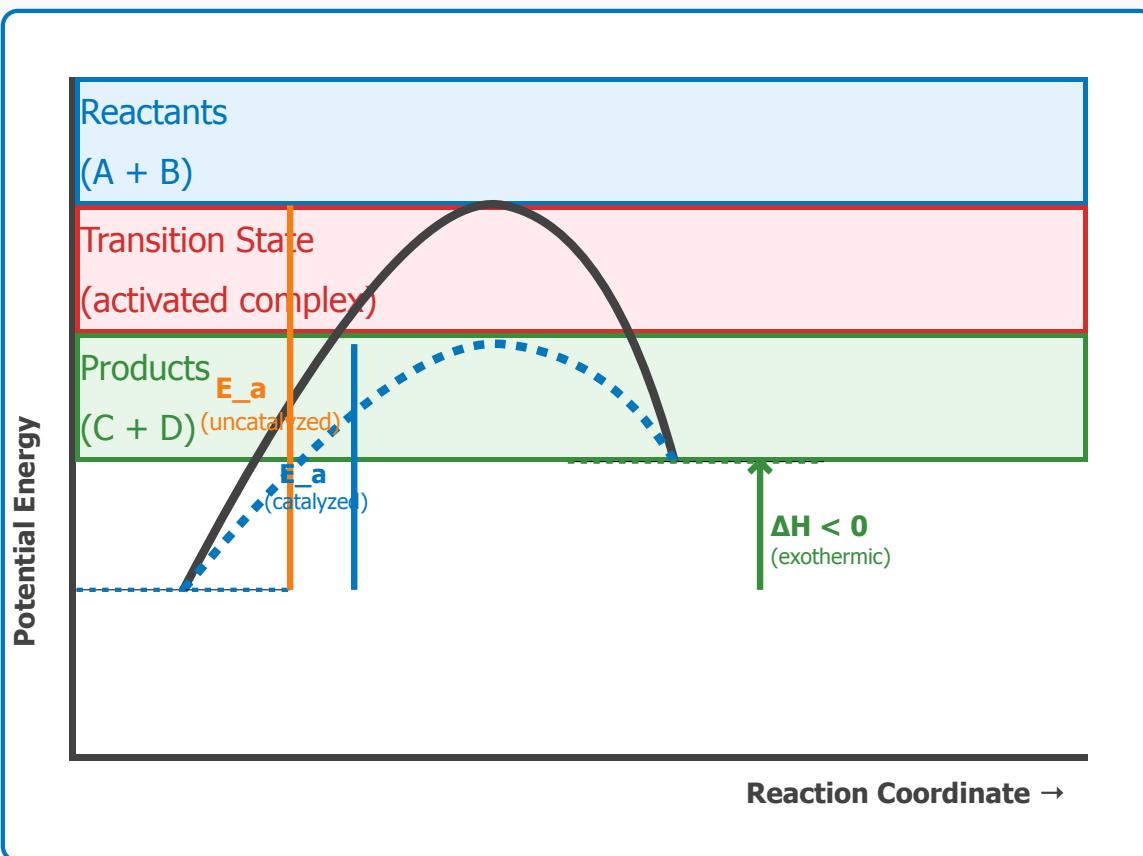
Work Space:

(d) Determine the **rate constant k** from the slope. Include units.

Work Space:

Question 6: Energy Diagram with Transition State (8 points)

The reaction $A + B \rightarrow C + D$ is exothermic ($\Delta H < 0$). The energy diagram below shows both the **uncatalyzed** and **catalyzed** pathways:



(a) On the diagram, identify the **activation energy (E_a)** for the uncatalyzed reaction. Is it the energy difference from reactants to the transition state, or from reactants to products?

Work Space:

(b) Explain why the **catalyzed pathway** (blue dashed line) has a **lower activation energy** than the uncatalyzed pathway (black solid line).

Work Space:

(c) Does the catalyst change the value of ΔH for the reaction?
Explain using the diagram.

Work Space:

(d) The **transition state** is shown at the peak of the curve. Why is it called an "activated complex," and why is it unstable?

Work Space:

Question 7: Reaction Mechanisms and Rate-Determining Step (9 points)

The reaction $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$ proceeds by the following two-step mechanism:

Step 1 (slow, rate-determining step):



NO₃ is an intermediate

Step 2 (fast):



(a) Add the two steps to obtain the **overall balanced equation**.

Show that the intermediate (NO₃) cancels out.

Work Space:

(b) Identify the **rate-determining step (RDS)**. How do you know which step is the RDS?

Work Space:

(c) Write the **rate law** for the overall reaction based on the rate-determining step.

Rule:

The rate law is determined by the slowest step. For Step 1: rate = $k[\text{NO}][\text{O}_2]$

Work Space:

(d) Suppose experimental data show that the reaction is second-order in NO and first-order in O₂ (rate = $k[NO]^2[O_2]$). Is this mechanism consistent with the experimental rate law? Explain.

Work Space:

Question 8: Arrhenius Equation and Activation Energy (9 points)

The rate constant k for a reaction is measured at two different temperatures:

Temperature (°C)	Temperature (K)	1/T (K ⁻¹)	k (s ⁻¹)	ln k
300	573	0.001746	1.5×10^{-3}	-6.50
400	673	0.001486	8.3×10^{-3}	-4.79

Arrhenius Equation (linearized) :

$$\ln k = -(\frac{E_a}{R})(\frac{1}{T}) + \ln A$$

Plot ln k vs. 1/T → slope = $-\frac{E_a}{R}$

(a) Calculate the **slope** of the $\ln k$ vs. $1/T$ line using the two data points. Use $\text{slope} = (y_2 - y_1)/(x_2 - x_1)$.

Work Space:

(b) Use the relationship $\text{slope} = -E_a/R$ to calculate the **activation energy E_a** . Use $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$. Report your answer in kJ/mol .

Steps:

1. $\text{slope} = -E_a/R$
2. $E_a = -\text{slope} \times R$
3. Convert J/mol to kJ/mol ($\div 1000$)

Work Space:

(c) Explain what the **activation energy** represents physically. Why do reactions with higher E_a proceed more slowly at the same temperature?

Work Space:

Question 9: Catalysis Conceptual Questions (4 points)

Answer the following questions about catalysts:

(a) A catalyst **lowers the activation energy** of a reaction. Does it lower E_a for the forward reaction only, or for both forward and reverse reactions? Explain.

Work Space:

(b) Does a catalyst appear in the **overall balanced equation**? Does it appear in the **rate law**? Explain the difference.

Work Space:

(c) A student claims: "Adding a catalyst will make an endothermic reaction become exothermic." Is this correct? Explain using energy diagrams.

Work Space:

Question 10: Conceptual Synthesis (4 points)

Answer the following conceptual questions:

(a) Explain why the **rate law cannot be determined** from the balanced equation alone (except for elementary reactions). What is the only way to determine the rate law?

Work Space:

(b) In a multi-step mechanism, an **intermediate** is formed in one step and consumed in a later step. Why must intermediates **not** appear in the overall equation or the final rate law?

Work Space:

END OF PRACTICE SET

Total: 75 points | Answer key begins on next page



COMPLETE ANSWER KEY & SCORING GUIDE

Question 1: Calculating Average Rate (6 points)

(a) Average rate of O₃ disappearance (3 points):

$$\text{Rate} = -\frac{\Delta[\text{O}_3]}{\Delta t} = -\frac{[\text{O}_3]_{\text{final}} - [\text{O}_3]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

$$= -\frac{0.028 \text{ M} - 0.040 \text{ M}}{12.0 \text{ s} - 0 \text{ s}} = -\frac{-0.012 \text{ M}}{12.0 \text{ s}} = 0.0010 \text{ M/s}$$

(1 pt for formula; 1 pt for substitution; 1 pt for answer with units)

(b) Average rate of O₂ formation (3 points):

From the balanced equation $2\text{O}_3 \rightarrow 3\text{O}_2$, the stoichiometric ratio is:

$$\frac{\text{Rate O}_2 \text{ formation}}{\text{Rate O}_3 \text{ disappearance}} = \frac{3}{2}$$

$$\text{Rate O}_2 \text{ formation} = \frac{3}{2} \times 0.0010 \text{ M/s} = 0.0015 \text{ M/s}$$

(1 pt for stoichiometric ratio; 1 pt for calculation; 1 pt for answer)

Scoring: (a) 3 pts; (b) 3 pts

Question 2: Initial Rate Method (10 points)

(a) Order with respect to A (2 points):

Compare Experiments 1 and 2 (where [B] is constant at 0.10 M):

[A] doubles: 0.10 → 0.20 (factor of 2)

Rate changes: $2.0 \times 10^{-3} \rightarrow 8.0 \times 10^{-3}$ (factor of 4 = 2²)

Since rate $\propto [A]^2$, the order with respect to A is **m = 2** (second-order). (2 pts)

(b) Order with respect to B (2 points):

Compare Experiments 1 and 3 (where [A] is constant at 0.10 M):

[B] doubles: 0.10 \rightarrow 0.20 (factor of 2)

Rate changes: $2.0 \times 10^{-3} \rightarrow 4.0 \times 10^{-3}$ (factor of 2 = 2^1)

Since rate $\propto [B]^1$, the order with respect to B is **n = 1** (first-order). (2 pts)

(c) Complete rate law (2 points):

$$\text{Rate} = k[A]^2[B]^1 = k[A]^2[B]$$

(1 pt for correct form; 1 pt for correct exponents)

(d) Rate constant k (3 points):

Using Experiment 1 data:

$$k = \frac{\text{Rate}}{[A]^2[B]} = \frac{2.0 \times 10^{-3} \text{ M/s}}{(0.10 \text{ M})^2(0.10 \text{ M})}$$

$$= \frac{2.0 \times 10^{-3}}{1.0 \times 10^{-3}} = 2.0 \text{ M}^{-2}\text{s}^{-1}$$

(1 pt for rearranging rate law; 1 pt for calculation; 1 pt for units)

(e) Overall reaction order (1 point):

Overall order = $m + n = 2 + 1 = 3$ (third-order overall). (1 pt)

Scoring: (a) 2 pts; (b) 2 pts; (c) 2 pts; (d) 3 pts; (e) 1 pt

Question 3: First-Order Half-Life (8 points)

(a) Half-life calculation (2 points):

$$\text{t}_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.21 \times 10^{-4}} \text{ years}^{-1} = 5727 \text{ years} \approx 5730 \text{ years}$$

(1 pt for formula and substitution; 1 pt for answer with units)

(b) Amount after one half-life (2 points):

After one half-life (5730 years), **half** of the original amount remains:

$$\text{Remaining} = \frac{100.0 \text{ g}}{2} = 50.0 \text{ g}$$

(1 pt for understanding; 1 pt for answer)

(c) Amount after two half-lives (2 points):

After two half-lives (11,460 years), the amount is halved twice:

$$\text{Remaining} = \frac{100.0 \text{ g}}{2^2} = \frac{100.0}{4} = 25.0 \text{ g}$$

(1 pt for understanding; 1 pt for answer)

(d) Why first-order $t_{1/2}$ is independent of $[A]_0$ (2 points):

For first-order reactions, $t_{1/2} = 0.693/k$, which **depends only on k** (the rate constant), not on $[A]_0$. (1 pt) This is because the rate is proportional to $[A]$, so as $[A]$ decreases, the rate slows proportionally—the *ratio* stays constant, giving a constant half-life. In zero-order reactions (rate = k), $t_{1/2} = [A]_0/(2k)$, which depends on $[A]_0$. In second-order (rate = $k[A]^2$), $t_{1/2} = 1/(k[A]_0)$, also dependent on $[A]_0$. (1 pt for comparison)

Scoring: (a) 2 pts; (b) 2 pts; (c) 2 pts; (d) 2 pts

Question 4: Concentration vs. Time Graphs (8 points)

(a) Zero-order equation and slope (2 points):

For zero-order kinetics, the integrated rate law is:

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

This is a linear equation ($y = mx + b$) where the **slope = $-k$** (negative rate constant). (1 pt for equation; 1 pt for slope identification)

(b) First-order constant half-life (2 points):

For first-order reactions, $t_{1/2} = 0.693/k$, which is **constant** (independent of $[A]$). (1 pt) This means no matter what the starting concentration is, it always takes the same amount of time to halve—hence the equal time intervals on the graph for $[A]$ to drop from $1.0 \rightarrow 0.5 \rightarrow 0.25 \rightarrow 0.125$, etc. (1 pt for explanation)

(c) Second-order increasing half-life (2 points):

For second-order reactions, $t_{1/2} = 1/(k[A]_0)$, which **increases** as $[A]$ decreases. (1 pt) As the reaction proceeds and $[A]$ gets smaller, it takes longer and longer to halve the remaining concentration—hence the increasing time intervals on the graph. The curve approaches the x-axis asymptotically. (1 pt for explanation)

(d) Verifying first-order by graphing (2 points):

To verify first-order, plot **ln[A] vs. time** on the y-axis. (1 pt) If the reaction is truly first-order, this plot will be linear with slope = $-k$, according to the integrated rate law $\ln[A]_t = -kt + \ln[A]_0$. (1 pt for reasoning)

Scoring: (a) 2 pts; (b) 2 pts; (c) 2 pts; (d) 2 pts

Question 5: Integrated Rate Law Graphing (9 points)

(a) Plot $\ln[H_2O_2]$ vs. time (3 points):

Plot the following points:

- (0 s, 0.00)
- (100 s, -0.49)
- (200 s, -0.99)
- (300 s, -1.47)
- (400 s, -1.97)

Draw a best-fit straight line through the points. (2 pts for accurate plotting; 1 pt for line)

(b) Linearity and reaction order (2 points):

Yes, the plot of $\ln[H_2O_2]$ vs. time is linear. (1 pt) This indicates the reaction is **first-order** with respect to H_2O_2 , because the first-order integrated rate law is $\ln[A]_t = -kt + \ln[A]_0$ (linear form). (1 pt)

(c) Slope calculation (2 points):

Using points (0 s, 0.00) and (400 s, -1.97):

$$\text{slope} = \frac{-1.97 - 0.00}{400 \text{ s} - 0 \text{ s}} = \frac{-1.97}{400} = -0.00493 \text{ s}^{-1}$$

(1 pt for calculation; 1 pt for units)

(d) Rate constant k (2 points):

Since slope = $-k$:

$$k = -(\text{slope}) = -(-0.00493 \text{ s}^{-1}) = 0.00493 \text{ s}^{-1} \approx 4.93 \times 10^{-3} \text{ s}^{-1}$$

(1 pt for relationship; 1 pt for answer with units)

Scoring: (a) 3 pts; (b) 2 pts; (c) 2 pts; (d) 2 pts

Question 6: Energy Diagram (8 points)

(a) Identifying E_a (2 points):

The **activation energy E_a** is the energy difference from **reactants to the transition state** (the peak of the curve), NOT from reactants to products. (1 pt) On the diagram, E_a is shown as the vertical arrow from the reactants energy level up to the top of the curve (transition state). (1 pt)

(b) Why catalyzed pathway has lower E_a (2 points):

A catalyst provides an **alternative reaction pathway** with a lower energy transition state. (1 pt) This lowers the activation energy barrier, allowing more molecules to have sufficient energy to react at a given temperature, thus increasing the reaction rate. The catalyst is not consumed and is regenerated at the end of the reaction. (1 pt)

(c) Does catalyst change ΔH? (2 points):

No, the catalyst does NOT change ΔH. (1 pt) ΔH is the energy difference between reactants and products (determined by the thermodynamics of bond breaking/forming). Both catalyzed and uncatalyzed pathways start at the same reactant energy level and end at the same product energy level, so ΔH remains the same. The catalyst only lowers the E_a (kinetic barrier), not the thermodynamic driving force. (1 pt for explanation using diagram)

(d) Transition state explanation (2 points):

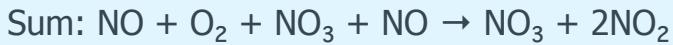
The transition state (activated complex) is the **highest energy configuration** along the reaction coordinate, where bonds are partially broken and partially formed. (1 pt) It's unstable because it exists only momentarily at the energy maximum—molecules either proceed forward to products or revert back to reactants. It cannot be isolated or observed directly. (1 pt)

Scoring: (a) 2 pts; (b) 2 pts; (c) 2 pts; (d) 2 pts

Question 7: Reaction Mechanisms (9 points)

(a) Overall equation (2 points):

Add the two steps:



Cancel NO_3 (intermediate, appears on both sides):



(1 pt for summing; 1 pt for canceling intermediate)

(b) Rate-determining step (2 points):

The **rate-determining step (RDS)** is **Step 1** ($\text{NO} + \text{O}_2 \rightarrow \text{NO}_3$). (1 pt)

We know it's the RDS because it's labeled "slow"—the slowest step in a mechanism controls the overall reaction rate, like the narrowest part of a funnel controlling flow. (1 pt)

(c) Rate law from RDS (2 points):

The rate law is determined by the rate-determining step (Step 1):



(1 pt for identifying RDS; 1 pt for correct rate law)

(d) Consistency with experimental rate law (3 points):

No, this mechanism is NOT consistent with the experimental rate law. (1 pt)

The mechanism predicts rate = $k[\text{NO}][\text{O}_2]$ (first-order in NO, first-order in O_2), but the experimental data show rate = $k[\text{NO}]^2[\text{O}_2]$ (second-order in NO, first-order in O_2). (1 pt) The mechanism is missing an additional NO dependence. A consistent mechanism would require Step 1 to be $2\text{NO} + \text{O}_2 \rightarrow$ (intermediate) or involve a fast pre-equilibrium with NO. (1 pt for explanation of inconsistency)

Scoring: (a) 2 pts; (b) 2 pts; (c) 2 pts; (d) 3 pts

Question 8: Arrhenius Equation (9 points)

(a) Slope calculation (3 points):

$$\text{slope} = \frac{\ln k_2 - \ln k_1}{(1/T_2) - (1/T_1)} = \frac{-4.79 - (-6.50)}{0.001486 - 0.001746}$$

$$= \frac{1.71}{-0.000260} = -6577 \text{ K}$$

(1 pt for formula; 1 pt for substitution; 1 pt for answer with units)

(b) Activation energy E_a (4 points):

From the Arrhenius equation: slope = $-E_a/R$

$$E_a = -(\text{slope}) \times R = -(-6577 \text{ K}) \times 8.314 \text{ J/(mol}\cdot\text{K)}$$

$$= 54,683 \text{ J/mol} = 54.7 \text{ kJ/mol}$$

(1 pt for relationship; 1 pt for calculation in J/mol; 1 pt for conversion to kJ/mol; 1 pt for final answer)

(c) Physical meaning of E_a (2 points):

The activation energy E_a is the **minimum energy** that reacting molecules must possess (as kinetic energy) to overcome the energy barrier and form the transition state, leading to products. (1 pt) Reactions with higher E_a require more energetic collisions to proceed—at a given temperature, fewer molecules have sufficient energy to react, so the reaction rate is slower.

Lowering E_a (e.g., with a catalyst) increases the fraction of molecules that can react. (1 pt)

Scoring: (a) 3 pts; (b) 4 pts; (c) 2 pts

Question 9: Catalysis Conceptual (4 points)

(a) Catalyst lowers E_a for both directions (1.5 points):

A catalyst lowers the activation energy for **both the forward and reverse reactions**. (1 pt) This is because the catalyst provides an alternative pathway that connects reactants and products through a lower-energy transition state, affecting both directions equally. (0.5 pt)

(b) Catalyst in equation vs. rate law (1.5 points):

A catalyst does **not** appear in the overall balanced equation because it is neither consumed nor produced (it's regenerated). (0.75 pt) However, it **may** appear in the rate law if it participates in the rate-determining step of the mechanism (e.g., in the slow step). For example, in enzyme catalysis, the rate law often includes the enzyme concentration. (0.75 pt)

(c) Catalyst does not change ΔH (1 point):

Incorrect. A catalyst does NOT change whether a reaction is endothermic or exothermic. ΔH is a thermodynamic property (energy difference between reactants and products) determined by bond energies, not by the reaction pathway. A catalyst only lowers E_a (kinetic barrier), making the reaction proceed faster, but the starting and ending energy levels (and thus ΔH) remain unchanged. (1 pt)

Scoring: (a) 1.5 pts; (b) 1.5 pts; (c) 1 pt

Question 10: Conceptual Synthesis (4 points)

(a) Rate law from experiment, not equation (2 points):

The balanced equation represents the **overall stoichiometry** but does NOT reveal the reaction mechanism (the sequence of elementary steps). (1 pt) Most reactions proceed through multi-step mechanisms, and the rate law depends on the slowest (rate-determining) step, NOT the overall equation. The **only way to determine the rate law** is through experimental measurement of how changing reactant concentrations affects the rate (initial rate method). (1 pt) (Exception: For elementary reactions—single-step processes—the rate law matches the stoichiometry.)

(b) Intermediates do not appear in overall equation or rate law (2 points):

Intermediates are species formed in one step and consumed in a later step—they **cancel out** when you add the mechanism steps to get the overall equation. (1 pt) They should not appear in the experimentally determined rate law because they are typically short-lived and their concentrations are not directly measurable or controllable. If an intermediate appears in the RDS-based rate law, it must be expressed in terms of reactants using pre-equilibrium or steady-state approximations. (1 pt)

Scoring: (a) 2 pts; (b) 2 pts