Week 14

AP Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

AP Chemistry Name: _____ Score: _____

1. A reactant drops from 0.9 M to 0.6 M in 5 s. The average rate (in M/s)?

   _____ M/s

2. For rate $= k[A]^2$, doubling $[A]$ multiplies the rate by...

   ☐ 4

   ☐ 2

   ☐ 8

3. If a plot of $\ln[A]$ versus time is a straight line, the reaction is...

   ☐ first order

   ☐ second order

   ☐ zero order

4. An intermediate is a species that is...

   ☐ made in one step and used up in a later one

   ☐ present at the start and end

   ☐ never involved in the reaction

5. Select **both** conditions a collision needs to cause a reaction.

   ☐ enough energy

   ☐ correct orientation

   ☐ a colour change

   Tick every correct option.

6. Reactants at 40 kJ, peak at 100 kJ. The activation energy (in kJ)?

   _____ kJ

7. The rate-determining step is the...

   ☐ slowest elementary step

   ☐ fastest elementary step

   ☐ last step

8. If the slow first step is $NO_2 + NO_2 \rightarrow$ products, the rate law is...

   ☐ rate $= k[NO_2]^2$

☐ rate $= k[NO_2]$

☐ rate $= k$

9. An intermediate is allowed to remain in the final rate law.

☐ True ☐ False

10. A first-order reaction starts at 16 M with a 10 s half-life. Concentration after 20 s (in M)?

_____ M

5. Kinetics

Answers · 答案

AP Chemistry

1. **0.06 M/s**

   Rate $= (0.9 - 0.6)/5 = 0.06$ M/s.

2. **4**

   Second order means $2^2 = 4$ times the rate.

3. **first order**

   A linear $\ln[A]$-versus-time plot indicates first order.

4. **made in one step and used up in a later one**

   An intermediate forms then is consumed, so it cancels overall.

5. **enough energy; correct orientation**

   A successful collision needs both sufficient energy and the right orientation.

6. **60 kJ**

   $E_a = 100 - 40 = 60$ kJ (peak minus reactants).

7. **slowest elementary step**

   The slowest step is the bottleneck controlling the overall rate.

8. **rate** $= k[\mathbf{NO_2}]^2$

   Two NO_2 react in the slow step, so it is second order.

9. **False**

   It must be substituted out using the fast equilibrium.

10. **4 M**

    Two half-lives give $16 \to 8 \to 4$ M.

AP CHEMISTRY • EXERCISE SHEET

5.1 How Fast a Reaction Goes

Name: _____ Class: _____ Date: _____ **Total: 10 marks**

KEY WORDS rate 反应速率 • catalyst 催化剂 • activation energy 活化能

Objective

Build the skills to answer exam questions on **reaction rate** — how fast a reaction goes and what changes it.

You must be able to:

- express **rate** 反应速率 as change in concentration per time
- list the factors that change rate (concentration, temperature, surface area, catalyst)
- explain each factor with collision ideas

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Rate as a change per time

The **rate** is how fast a reactant is used up or a product forms:

$$\text{rate} = \frac{\Delta[\text{concentration}]}{\Delta t},$$

usually in mol $L^{-1}s^{-1}$.

■ Factors that speed up a reaction

- **Higher concentration** — more particles per volume ⇒ more collisions.
- **Higher temperature** — faster particles, and more with enough energy.
- **Larger surface area** — more exposed particles to collide with.
- **A catalyst** — a lower-energy pathway.

■ The collision picture

A reaction happens when particles **collide** with enough energy and the right orientation. Anything that increases the **frequency** or **energy** of successful collisions speeds the reaction.

■ Reading a rate from a graph

On a concentration-vs-time graph, the rate is the **slope**. The reaction is fastest at the start (steepest) and slows as reactants run out.

2 Practice

Now apply the methods above.

2.1 Write the definition of reaction rate. [1]

2.2 State two factors that increase reaction rate. [2]

2.3 Why does a powder react faster than a lump of the same mass? [1]

3 Exam-style questions

3.1 Increasing the concentration of a reactant increases the rate because it [1]

- **A** lowers the activation energy
- **B** increases the collision frequency
- **C** changes the products
- **D** cools the mixture

3.2 A reaction is run at 20°C and again at 40°C.

(a) State which is faster. [1]

(b) Give two reasons, in terms of particle collisions, why raising temperature speeds a reaction. [2]

3.3 Explain, using collision ideas, why a catalyst speeds up a reaction without being used

up. [2]

Solutions

2.1 The change in concentration of a reactant or product per unit time.

2.2 Any two: higher concentration, higher temperature, larger surface area, a catalyst.

2.3 A powder has a larger surface area, so more particles are exposed to collide.

3.1 B — more particles per volume means more frequent collisions.

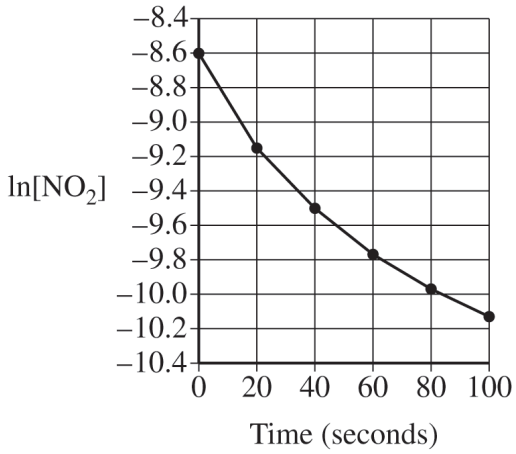
3.2 (a) 40°C. (b) Particles move faster (more frequent collisions) and more of them have energy above the activation energy (more successful collisions).

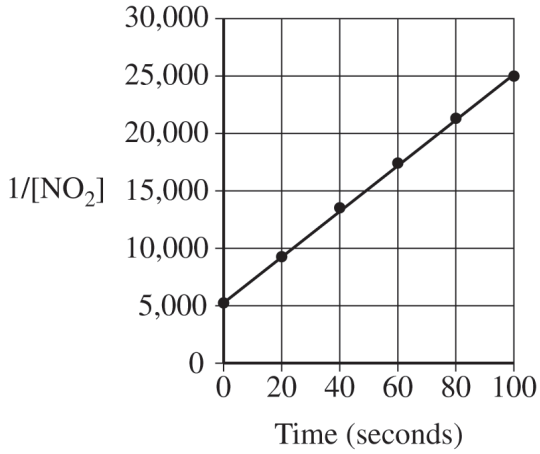
3.3 A catalyst provides an alternative pathway with a lower activation energy, so more collisions succeed; it is regenerated at the end, so it is not consumed.

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.





Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.

(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7}\ M/s$.

Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

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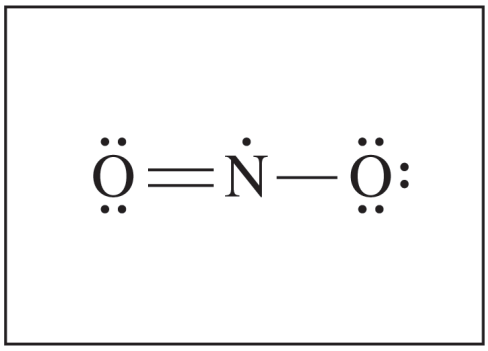
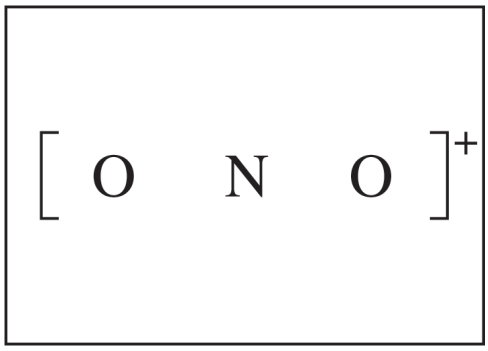
Continue your response to **QUESTION 6** on this page.

(c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2, the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.





(i) In the box on the right, complete the Lewis diagram for NO_2^+. Be sure to show all bonding and nonbonding electrons.

(ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

. Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

(a) Write the balanced net ionic equation for the reaction.

A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $HCl(aq)$ at 21.2° C with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

Trial	Concentration of $HCl(aq)$ (M)	Particle Size of $CaCO_3(s)$	Time of Reaction (s)
1	1.00	Fine powder	67
2	1.00	Small chunks	112
3	1.00	Large chunk	342
4	3.00	Fine powder	22
5	3.00	Small chunks	227
6	3.00	Large chunk	114

(b) The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

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Continue your response to **QUESTION 3** on this page.

(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

(d) The student claims that the reaction is zero order with respect to $HCl(aq)$. Do you agree or disagree with the student's claim? Justify your answer using the student's data.

(e) The $HCl(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $HCl(aq)$ in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of $CaCO_3$ is 100.09 g/mol.)

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Continue your response to **QUESTION 5** on this page.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Time (s)	Measured Temperature of Solution (° C)
0	21.20
20	21.51
40	21.70
60	21.85
80	21.90
100	21.90

(f) Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(g) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is $4.0\ \text{J} / (\text{g} \cdot {}^\circ\text{C})$.

(i) Calculate the magnitude of heat transfer, q, in joules.

(ii) Calculate the enthalpy of reaction in units of kJ/mol_{rxn}. Include the algebraic sign on your answer.

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AP CHEMISTRY • EXERCISE SHEET

5.2 Writing the Rate Law

Name: _____ Class: _____ Date: _____ **Total: 12 marks**

KEY WORDS order 级数 • rate law 速率定律 • rate constant 速率常数

Objective

Build the skills to answer exam questions on the **rate law** — how rate depends on concentration.

You must be able to:

- write a **rate law** 速率定律 rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$
- find the **order** 级数 with respect to each reactant from data
- calculate the **rate constant** k

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The rate law

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n,$$

where m and n are the **orders** (found by experiment, not from coefficients) and k is the rate constant.

■ Finding order by comparing experiments

Change one reactant's concentration and see how the rate responds:

- rate unchanged when [A] doubles → order 0 in A;
- rate doubles → order 1;
- rate quadruples (×4) → order 2.

■ A worked order

If doubling [A] (with [B] fixed) makes the rate 4× larger, then $2^m = 4$, so $m = 2$ (second order in A).

■ Finding k

Substitute one experiment's rate and concentrations into the rate law and solve for k. Its units depend on the overall order.

2 Practice

Now apply the methods above.

2.1 In rate $= k[\mathrm{A}]^2[\mathrm{B}]$, state the order in A and in B. [2]

2.2 Doubling [A] doubles the rate. What is the order in A? [1]

2.3 Are reaction orders taken from the balanced equation? [1]

3 Exam-style questions

3.1 If doubling a reactant's concentration quadruples the rate, the order is [1]

- **A** 0
- **B** 1
- **C** 2
- **D** 3

3.2 For $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$, experiments give:

exp	[A]	[B]	rate
1	0.1	0.1	2
2	0.2	0.1	4
3	0.1	0.2	8

(a) Find the order in A and in B. [3]

(b) Write the rate law. [1]

3.3 Using experiment 1 above (rate = 2, [A] = [B] = 0.1) and your rate law, find k. [3]

Solutions

2.1 Second order in A; first order in B.

2.2 First order.

2.3 No — orders are found by experiment.

3.1 C — $2^m = 4 \Rightarrow m = 2$.

3.2 (a) A: exp 1→2 doubles [A], rate doubles → order 1; B: exp 1→3 doubles [B], rate ×4 → order 2. (b) rate = $k[\text{A}][\text{B}]^2$.

3.3 $2 = k(0.1)(0.1)^2 = k(0.001)$; $k = 2000\ \text{L}^2\text{mol}^{-2}\text{s}^{-1}$.

2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O.

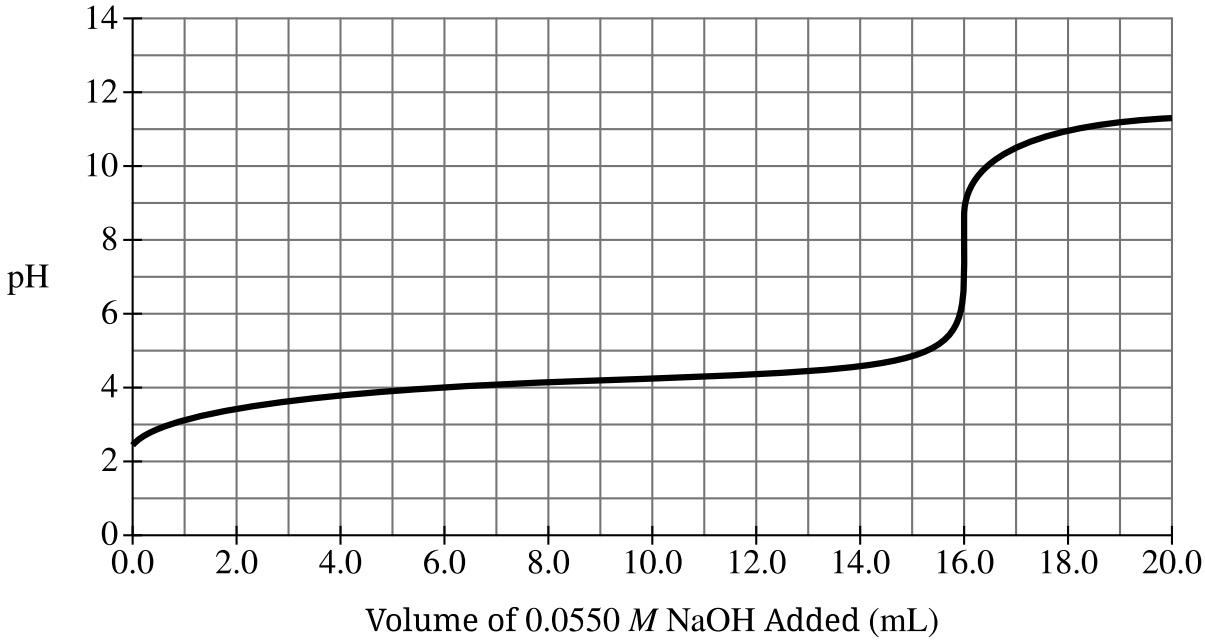
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $HAsc(aq)$, acts as a weak acid, as shown in the equation.

$$HAsc(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Asc^-(aq)$$

The following titration curve was produced when a 10.0 mL sample of $HAsc(aq)$ was titrated using $0.0550\ M\ NaOH(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate pK_a of ascorbic acid.

iii. What is the value of the ratio $\frac{[Asc^-]}{[HAsc]}$ when the pH of the solution is 4.7?

C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^-, as represented by the following equation.

$$HAsc + I_3^- \rightarrow DHAsc + 3\,I^- + 2\,H^+$$

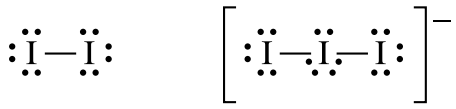
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^-, producing the following data.

Trial	[HAsc] (M)	$[I_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

i. The rate law for the reaction is $rate = k[HAsc][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[HAsc]$.

ii. Calculate the value of the rate constant, *k*, for the reaction. Include units with your answer.

D. The triiodide ion, I_3^-, is significantly more soluble in water than elemental iodine, I_2, is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



I_2 $\qquad\qquad$ I_3^-

. Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

(a) Write the balanced net ionic equation for the reaction.

A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $HCl(aq)$ at 21.2° C with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

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(b) The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

(d) The student claims that the reaction is zero order with respect to $HCl(aq)$. Do you agree or disagree with the student's claim? Justify your answer using the student's data.

(e) The $HCl(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $HCl(aq)$ in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of $CaCO_3$ is 100.09 g/mol.)

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Continue your response to **QUESTION 6** on this page.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Time (s)	Measured Temperature of Solution (° C)
0	21.20
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100	21.90

(f) Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(g) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is $4.0\ \text{J} / (\text{g} \cdot {}^\circ\text{C})$.

(i) Calculate the magnitude of heat transfer, q, in joules.

(ii) Calculate the enthalpy of reaction in units of kJ/mol_{rxn}. Include the algebraic sign on your answer.

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. The following equation represents the decomposition of N_2O_5, for which the rate law is rate = $k[N_2O_5]$.

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

A sample of pure $N_2O_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $N_2O_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[N_2O_5](M)$
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

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

(b) The following mechanism is proposed for the decomposition of $N_2O_5(g)$.

Step 1: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$
Step 2: $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$
Step 3: $N_2O_5(g) + NO(g) \rightarrow 3\ NO_2(g)$

Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

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Continue your response to **QUESTION 5** on this page.

(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5, would the value of k increase, decrease, or remain the same? Explain your reasoning.

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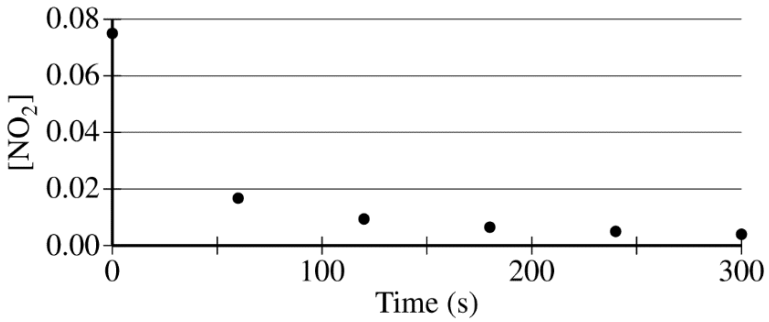
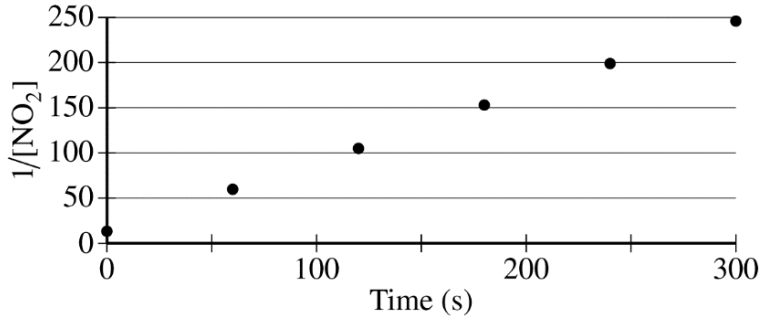
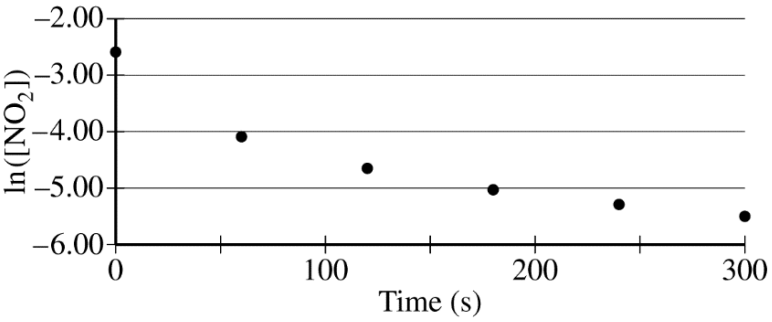
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

Step 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

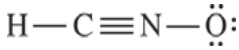
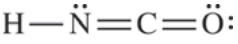
Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
	

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

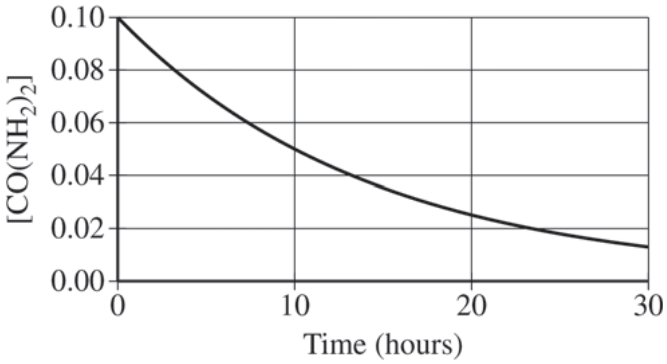
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

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

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea 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



(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

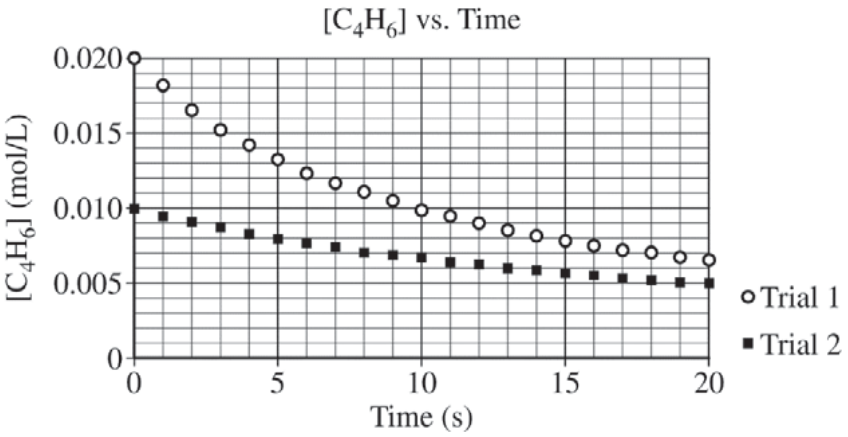
(i) Explain how the data support the student's proposed rate law.

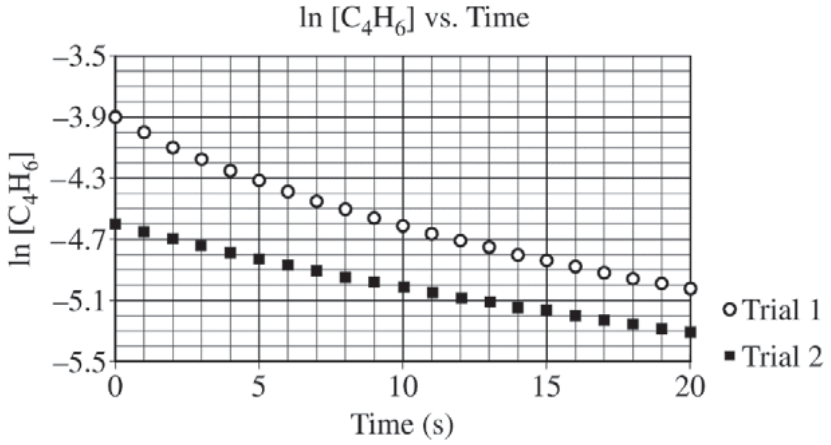
(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

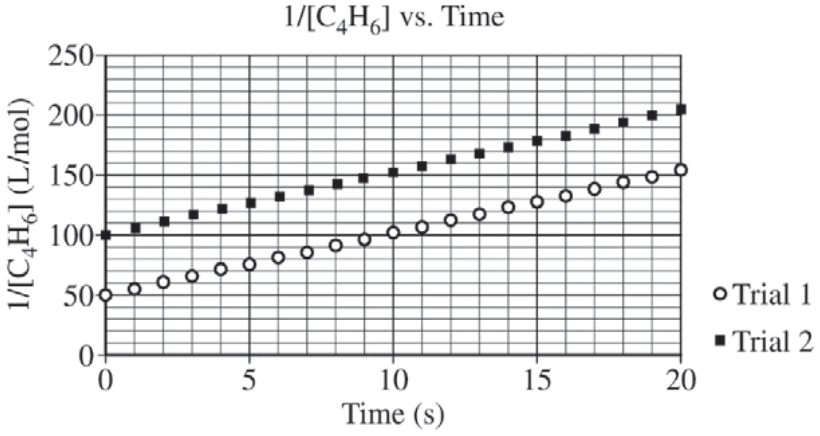
(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

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

5. At high temperatures the compound C_4H_6 (1,3-butadiene) 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.







(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.

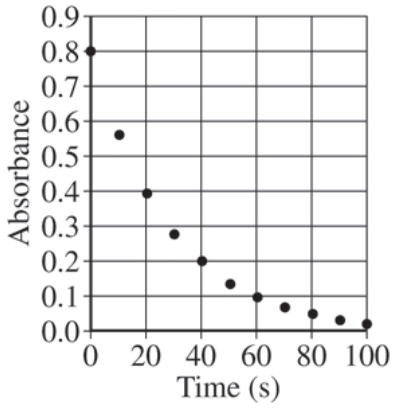
(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L·s). Calculate the rate constant, k, for the reaction at 625 K.

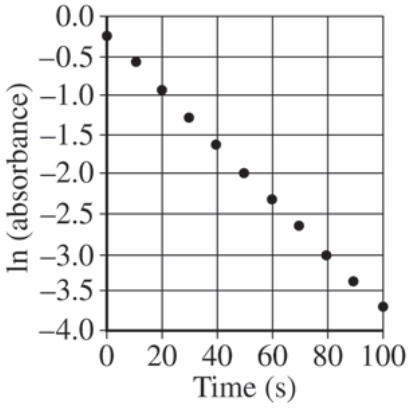
AP Chemistry: **2015**

$$\underset{\textit{blue}}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \rightarrow \underset{\textit{colorless}}{\text{products}}$$

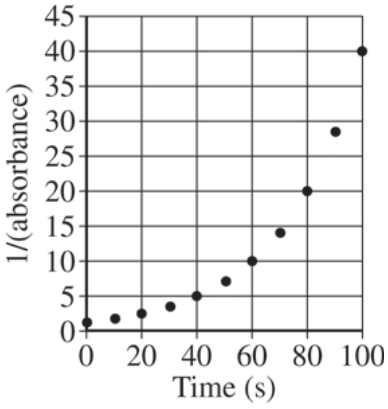
5. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II



Graph III

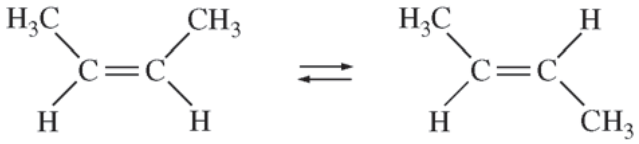
(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

(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 near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

(c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?



cis-2-butene ⇌ *trans*-2-butene

7. The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

STOP

END OF EXAM

AP CHEMISTRY • EXERCISE SHEET

5.3 Concentration Over Time

Name: _____ Class: _____ Date: _____ **Total: 11 marks**

KEY WORDS half-life 半衰期 • rate constant 速率常数 • rate law 速率方程

Objective

Build the skills to answer exam questions on **concentration over time** — the integrated rate laws.

You must be able to:

- recognise a **zero, first, or second order** reaction from a straight-line plot
- use the **half-life** 半衰期 of a first-order reaction
- know which graph is linear for each order

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Which plot is linear

- **Zero order**: [A] vs t is a straight line.
- **First order**: ln[A] vs t is a straight line.
- **Second order**: $\frac{1}{[\mathrm{A}]}$ vs t is a straight line.

Test data by seeing which plot gives a straight line — that reveals the order.

■ The slope gives k

For first order, $\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$: the slope is $-k$. For second order, the slope of $\frac{1}{[\mathrm{A}]}$ vs t is $+k$.

■ First-order half-life

A first-order reaction has a **constant** half-life:

$$t_{1/2} = \frac{0.693}{k}.$$

It takes the same time to halve, over and over — independent of the starting amount.

■ **A worked half-life**

If $k = 0.0347\ \text{s}^{-1}$, then $t_{1/2} = \dfrac{0.693}{0.0347} = 20\ \text{s}$.

2 Practice

Now apply the methods above.

2.1 Which plot is linear for a first-order reaction? [1]

2.2 Find the half-life of a first-order reaction with $k = 0.100\ \text{s}^{-1}$. [2]

2.3 For a first-order reaction, does the half-life depend on the starting concentration? [1]

3 Exam-style questions

3.1 A plot of $\dfrac{1}{[\text{A}]}$ vs time is linear. The reaction is [1]

- **A** zero order
- **B** first order
- **C** second order
- **D** third order

3.2 A first-order reaction has a half-life of 30 s.

(a) Find the rate constant k. [2]

(b) What fraction of the reactant remains after 60 s? [2]

3.3 A student plots [A], ln[A], and $\frac{1}{[A]}$ against time; only the ln[A] plot is straight. State the order and how to find k from the graph. [2]

Solutions

2.1 ln[A] vs t.

2.2 $t_{1/2} = \dfrac{0.693}{0.100} = 6.93$ s.

2.3 No — it is constant (independent of starting concentration).

3.1 C — a linear $\frac{1}{[\text{A}]}$ plot means second order.

3.2 (a) $k = \dfrac{0.693}{30} = 0.0231\ \text{s}^{-1}$. (b) 60 s is two half-lives, so $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$ remains.

3.3 First order; the slope of the ln[A] vs t line is $-k$.

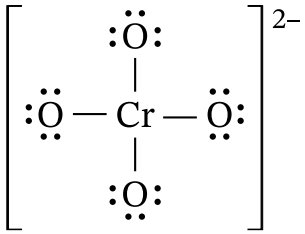
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

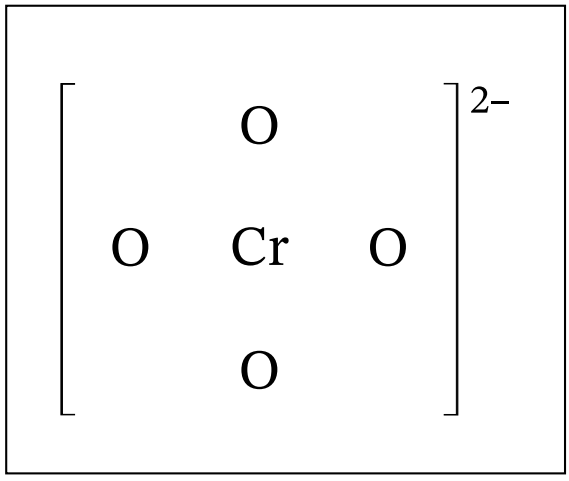
Figure 1



i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

ii. On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of −1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

Figure 2



Part B

When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

Part C

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

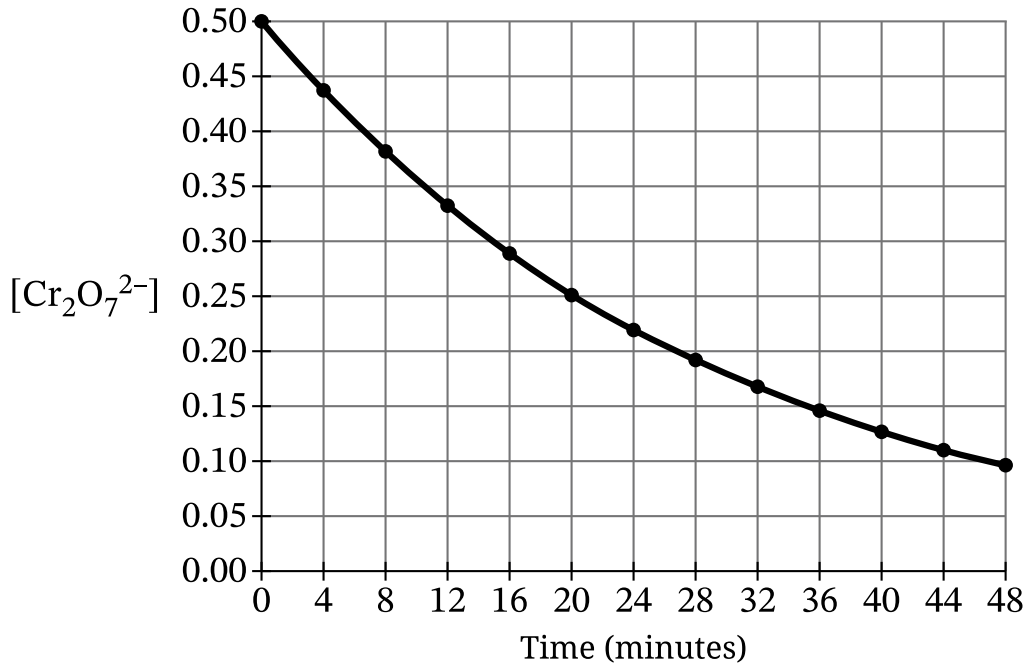
Part D

Calculate the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when $15.0\ \text{A}$ of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

In a separate experiment, an iron wire is placed directly in a solution of $0.50\ M\ Cr_2O_7^{2-}(aq)$ with $pH = 1.99$. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

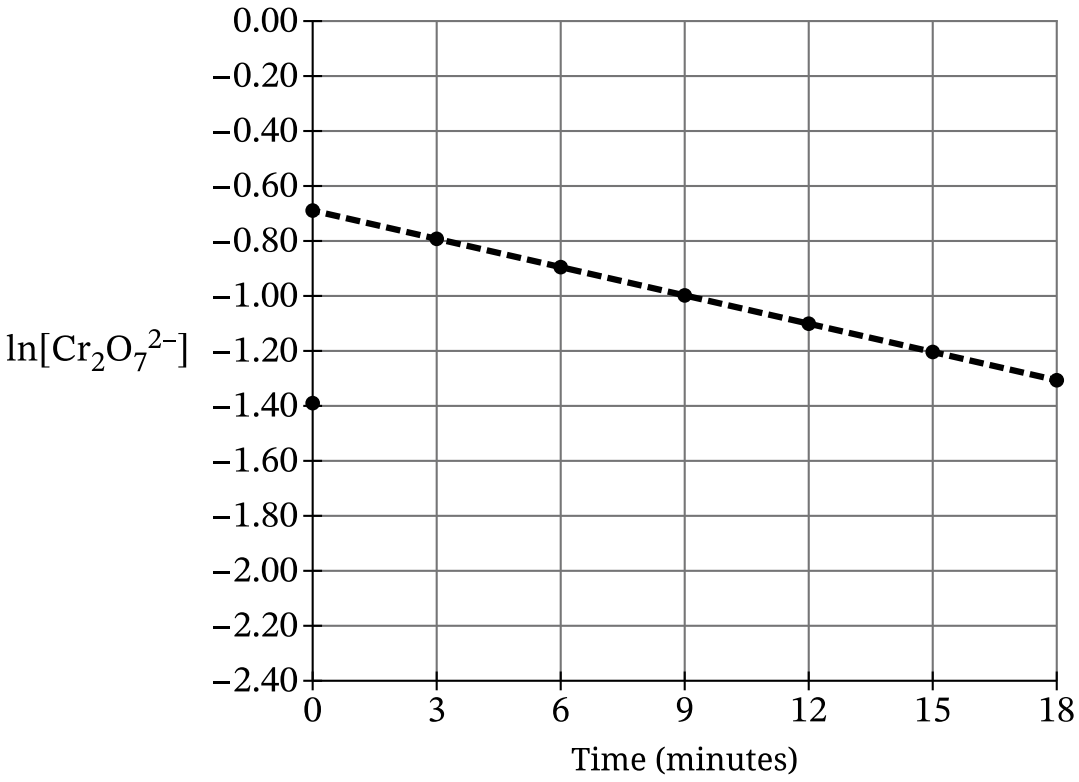


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time for a trial with an initial concentration of $0.50\ M\ Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

Figure 4



Part F

Calculate the value of the rate constant, *k*, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

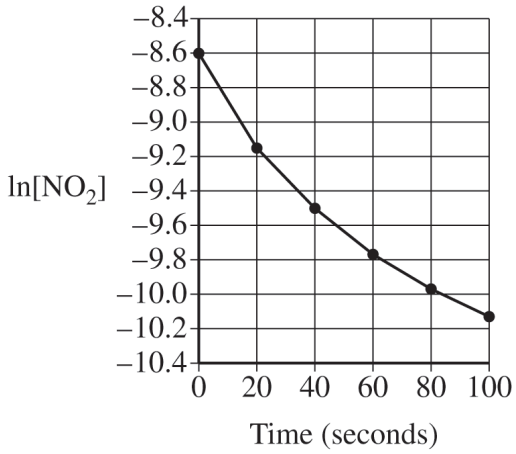
Part G

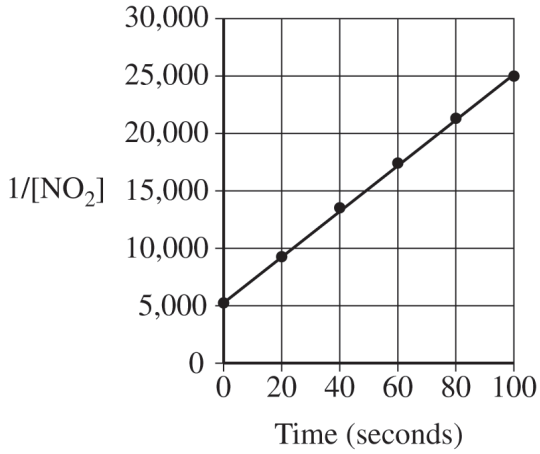
The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of $0.25\ M\ Cr_2O_7^{2-}(aq)$ instead of $0.50\ M\ Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.





Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.

(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

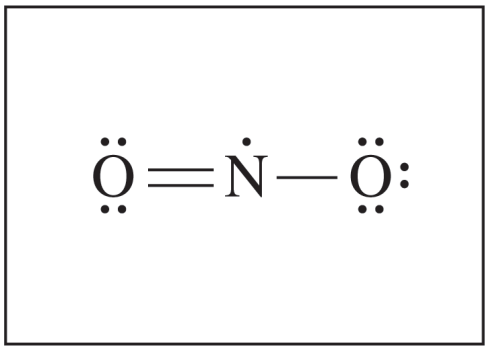
(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7}\ M/s$.

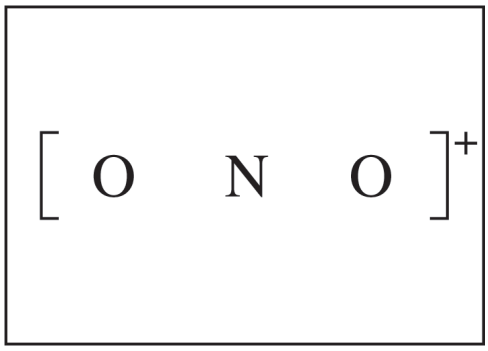
Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 6** on this page.

(c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2, the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.





(i) In the box on the right, complete the Lewis diagram for NO_2^+. Be sure to show all bonding and nonbonding electrons.

(ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

. The following equation represents the decomposition of N_2O_5, for which the rate law is rate = $k[N_2O_5]$.

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

A sample of pure $N_2O_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $N_2O_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[N_2O_5](M)$
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

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

(b) The following mechanism is proposed for the decomposition of $N_2O_5(g)$.

Step 1: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$
Step 2: $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$
Step 3: $N_2O_5(g) + NO(g) \rightarrow 3\ NO_2(g)$

Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 5** on this page.

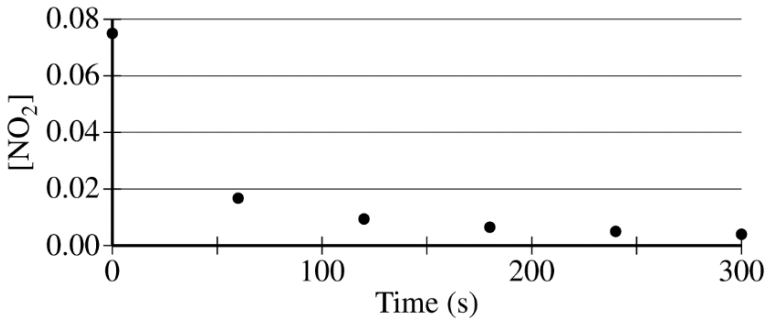
(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5, would the value of k increase, decrease, or remain the same? Explain your reasoning.

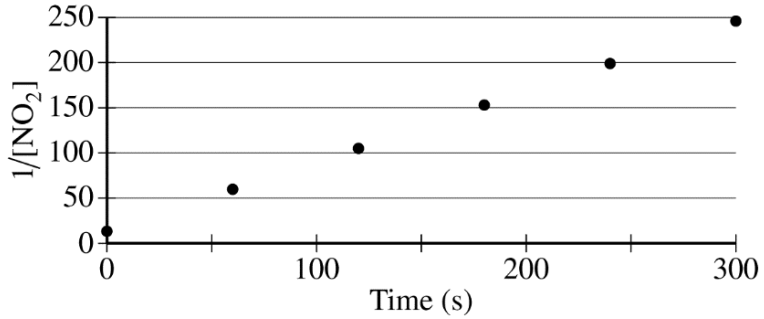
GO ON TO THE NEXT PAGE.

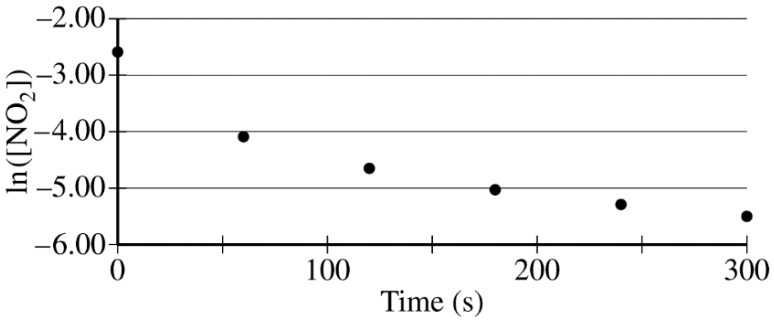
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ *slow*

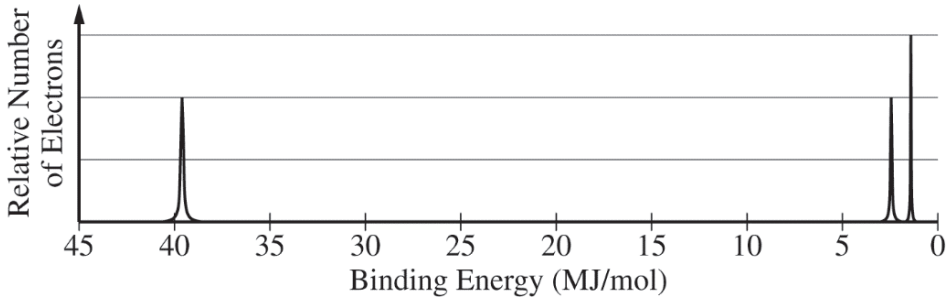
Step 2: $NO_3(g) \rightarrow NO(g) + O_2(g)$ *fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

Step 1: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

Step 2: $N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$ *slow*



7. The complete photoelectron spectrum of an element is represented above.

   (a) Identify the element.

   A radioactive isotope of the element decays with a half-life of 10. minutes.

   (b) Calculate the value of the rate constant, k, for the radioactive decay. Include units with your answer.

   (c) If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

STOP

END OF EXAM

2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

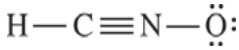
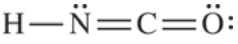
Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
	

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

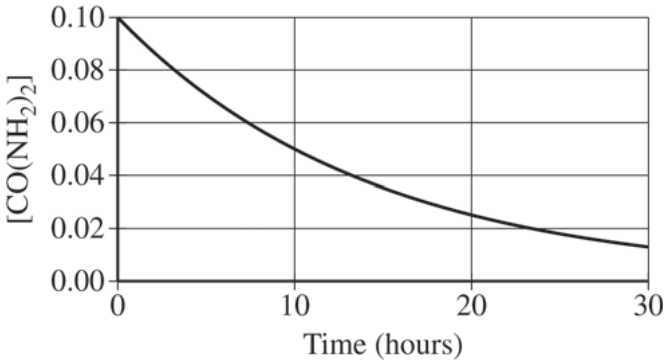
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

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

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea 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



(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

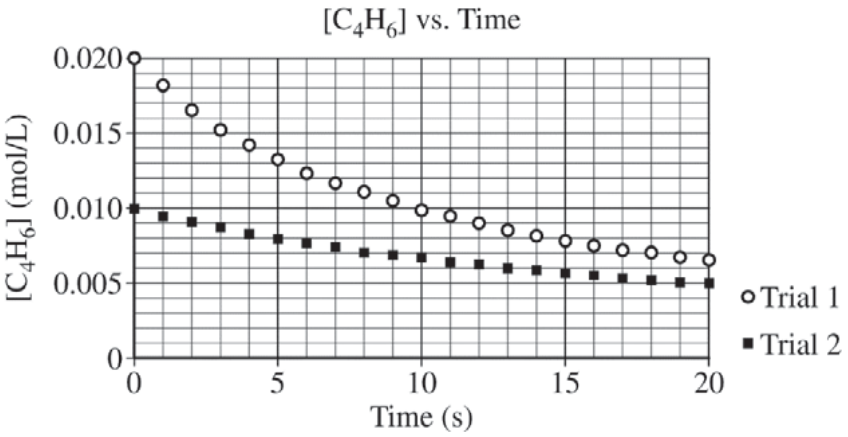
(i) Explain how the data support the student's proposed rate law.

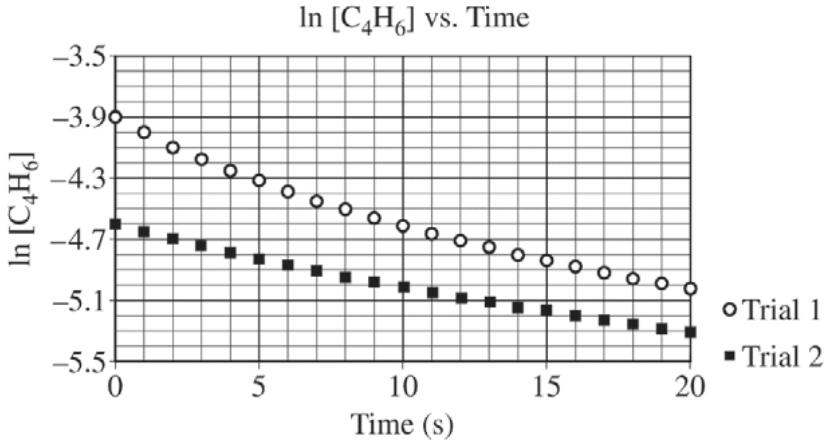
(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

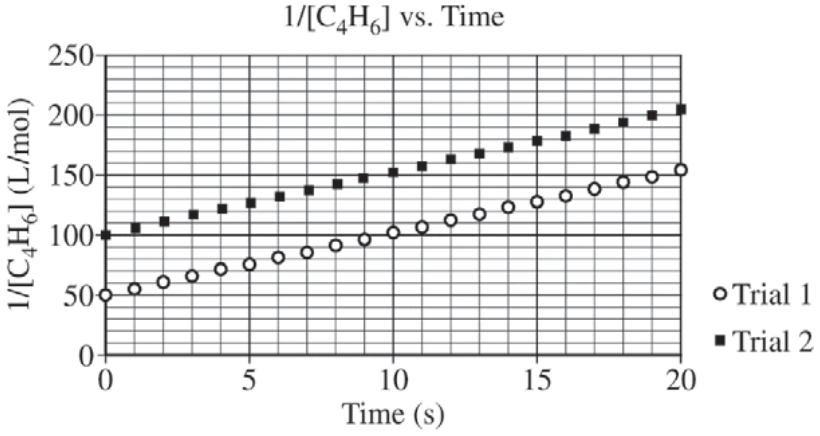
(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

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

5. At high temperatures the compound C_4H_6 (1,3-butadiene) 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.







(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) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L·s). Calculate the rate constant, k, for the reaction at 625 K.

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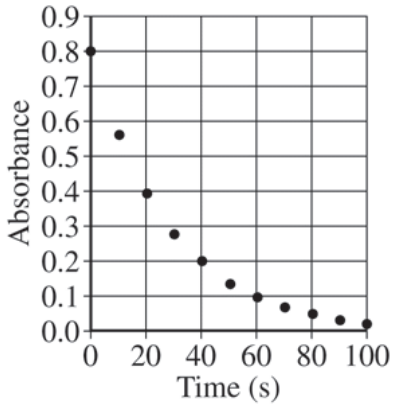
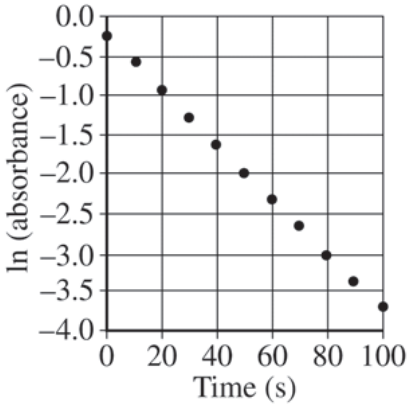
$$\underset{\textit{blue}}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \rightarrow \underset{\textit{colorless}}{\text{products}}$$

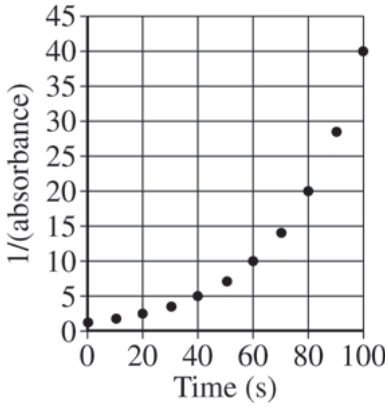
5. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II



Graph III

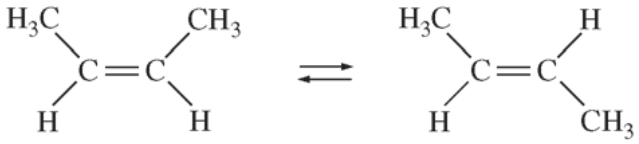
(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

(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 near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

(c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?



cis-2-butene *trans*-2-butene

7. The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

STOP

END OF EXAM

AP CHEMISTRY • EXERCISE SHEET

5.4 The Steps a Reaction Really Takes

Name: _____ Class: _____ Date: _____ **Total: 9 marks**

KEY WORDS mechanism 反应机理 • elementary steps 基元反应 • intermediates 中间体 • rate law 速率方程 • catalyst 催化剂

Objective

Build the skills to answer exam questions on **reaction mechanisms** — the real steps a reaction takes.

You must be able to:

- describe a **mechanism** 反应机理 as a sequence of **elementary steps** 基元反应
- identify **intermediates** 中间体 (made then used up)
- use **molecularity** to write an elementary step's rate law

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ A mechanism is a sequence of steps

Most reactions happen in several **elementary steps**, not one giant collision. The steps must add up to the overall balanced equation.

■ Intermediates

An **intermediate** is produced in one step and consumed in a later one, so it does **not** appear in the overall equation. (A catalyst is the reverse — used first, regenerated later.)

■ Molecularity gives the step's rate law

For an **elementary** step (and only for elementary steps) the rate law uses the coefficients directly:

- A $\rightarrow$ products: rate $= k[\mathrm{A}]$;
- A + B $\rightarrow$: rate $= k[\mathrm{A}][\mathrm{B}]$;
- 2A $\rightarrow$: rate $= k[\mathrm{A}]^2$.

■ **Checking a mechanism**

Add the steps: intermediates should cancel, leaving the overall equation. Only then is the mechanism valid.

2 Practice

Now apply the methods above.

2.1 What is an intermediate? [1]

2.2 Write the rate law for the elementary step $A + B \rightarrow C$. [1]

2.3 In a two-step mechanism, a species is made in step 1 and used in step 2. Name it. [1]

3 Exam-style questions

3.1 For an **elementary** step $2NO \rightarrow N_2O_2$, the rate law is [1]

- **A** $k[NO]$
- **B** $k[NO]^2$
- **C** $k[N_2O_2]$
- **D** k

3.2 A mechanism is: Step 1 $A \rightarrow X$; Step 2 $X + B \rightarrow C$.

(a) Identify the intermediate. [1]

(b) Write the overall equation. [2]

3.3 Explain why you cannot write the rate law of an **overall** reaction directly from its

coefficients, but you can for an elementary step. [2]

Solutions

2.1 A species made in one step and consumed in a later step (not in the overall equation).

2.2 rate = k[A][B].

2.3 An intermediate.

3.1 B — an elementary step's rate law uses its coefficients: $k[\mathrm{NO}]^2$.

3.2 (a) X. (b) Adding the steps, X cancels: $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$.

3.3 The overall equation may hide several steps, so its coefficients need not match the true dependence; an elementary step **is** a single collision event, so its molecularity gives its rate law directly.

AP CHEMISTRY • EXERCISE SHEET

5.5 Why Collisions Do or Do Not React

Name: _____ Class: _____ Date: _____ **Total: 11 marks**

KEY WORDS activation energy 活化能 • orientation 取向 • collision theory 碰撞理论 • reaction rate 反应速率

Objective

Build the skills to answer exam questions on **collision theory** — why some collisions react and others do not.

You must be able to:

- state the two requirements for a successful collision (**energy** and **orientation** 取向)
- define **activation energy** 活化能 E_a
- link temperature to the fraction of successful collisions

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Two requirements

For a collision to react, the particles must collide with:

1. at least the **activation energy** E_a (enough energy to break bonds), and
2. the correct **orientation** (the right parts must meet).

Most collisions fail one of these, so only a fraction react.

■ Activation energy

E_a is the **minimum energy** needed to start the reaction — the barrier that must be climbed before products form.

■ Temperature and successful collisions

Raising temperature gives particles more kinetic energy, so a **larger fraction** exceed E_a. This is the main reason a small temperature rise can greatly speed a reaction.

■ The Maxwell-Boltzmann link

On the speed distribution, the molecules to the right of E_a can react. Heating shifts the curve right, moving **more** molecules past E_a.

2 Practice

Now apply the methods above.

2.1 State the two requirements for a successful collision. [2]

2.2 Define activation energy. [1]

2.3 Why does raising temperature increase the fraction of successful collisions? [1]

3 Exam-style questions

3.1 The activation energy is the [1]

- **A** energy released by the reaction
- **B** minimum energy needed for a collision to react
- **C** average energy of the particles
- **D** energy of the products

3.2 Two gas molecules collide but do not react.

(a) Give two possible reasons. [2]

(b) Explain how heating the gas would increase the reaction rate. [2]

3.3 On a Maxwell-Boltzmann distribution, explain what the area to the **right** of E_a

represents and how it changes with temperature. [2]

Solutions

2.1 Enough energy (at least E_a); correct orientation.

2.2 The minimum energy needed for a collision to lead to reaction.

2.3 Particles have more kinetic energy, so more of them exceed E_a.

3.1 B — the minimum energy for a collision to react.

3.2 (a) Not enough energy (below E_a); wrong orientation. (b) Heating raises particle energy, so more collisions exceed E_a and collisions are more frequent, increasing the rate.

3.3 It represents the fraction of molecules with energy $\geq E_a$ (able to react); heating shifts the curve right so this area grows.

2. A chemical reaction between maleic acid $(H_2C_4H_2O_4)$ and sodium bicarbonate $(NaHCO_3)$ occurs in the presence of water to produce carbon dioxide and sodium maleate $(Na_2C_4H_2O_4)$, as represented by the following equation.

$$H_2C_4H_2O_4(aq) + 2\,NaHCO_3(aq) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) + Na_2C_4H_2O_4(aq)$$

(a) A student combines equal masses of $H_2C_4H_2O_4(s)$ chunks and $NaHCO_3(s)$ chunks with sufficient water at 20.0°C. The student determines that 0.0114 mol of $CO_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $CO_2(g)$ produced.

(ii) The $CO_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm. Calculate the volume of $CO_2(g)$, in liters.

(b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $H_2C_4H_2O_4(s)$ and $NaHCO_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

(iii) When the reaction is complete, will the volume of $CO_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $H_2C_4H_2O_4$ (grams)	Mass of $NaHCO_3$ (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

(c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

(d) The reaction has a value of $\Delta S°$ greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

(e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S^\circ_{rxn} > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.

$$H_2C_4H_2O_4 + H_2O \rightleftarrows HC_4H_2O_4^- + H_3O^+ \qquad K_{a_1} = 1.5 \times 10^{-2}$$

$$HC_4H_2O_4^- + H_2O \rightleftarrows C_4H_2O_4^{2-} + H_3O^+ \qquad K_{a_2} = 8.5 \times 10^{-7}$$

(f) Calculate the pK_{a_2} value for the $HC_4H_2O_4^-$ ion.

(g) A buffer solution with a pH of 7.00 is prepared using $C_4H_2O_4^{2-}$ and $HC_4H_2O_4^-$. Calculate the ratio

$\dfrac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^-]}$ in this solution.

GO ON TO THE NEXT PAGE.

. Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

(a) Write the balanced net ionic equation for the reaction.

A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $HCl(aq)$ at 21.2° C with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

Trial	Concentration of $HCl(aq)$ (M)	Particle Size of $CaCO_3(s)$	Time of Reaction (s)
1	1.00	Fine powder	67
2	1.00	Small chunks	112
3	1.00	Large chunk	342
4	3.00	Fine powder	22
5	3.00	Small chunks	227
6	3.00	Large chunk	114

(b) The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

(d) The student claims that the reaction is zero order with respect to $HCl(aq)$. Do you agree or disagree with the student's claim? Justify your answer using the student's data.

(e) The $HCl(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $HCl(aq)$ in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of $CaCO_3$ is 100.09 g/mol.)

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 6** on this page.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Time (s)	Measured Temperature of Solution (° C)
0	21.20
20	21.51
40	21.70
60	21.85
80	21.90
100	21.90

(f) Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(g) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is $4.0\ \text{J} / (\text{g} \cdot {}^\circ\text{C})$.

(i) Calculate the magnitude of heat transfer, q, in joules.

(ii) Calculate the enthalpy of reaction in units of kJ/mol_{rxn}. Include the algebraic sign on your answer.

GO ON TO THE NEXT PAGE.

CHEMISTRY

Section II

7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

$$CS_2(g) + 3\ Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(g)$$

1. Carbon tetrachloride, $CCl_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.

   (a) Chlorine gas, $Cl_2(g)$, is initially present in the container at a pressure of 0.40 atm.

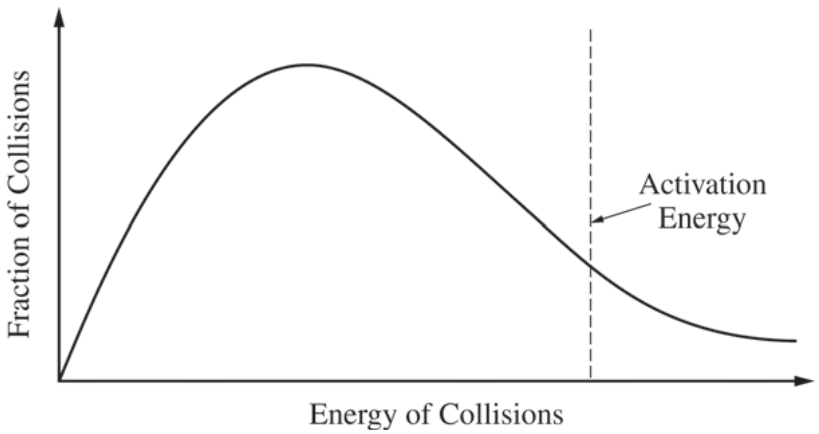
   (i) How many moles of $Cl_2(g)$ are in the container?

   (ii) How many grams of carbon disulfide, $CS_2(g)$, are needed to react completely with the $Cl_2(g)$?

   (b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C, the reaction occurs at an observable rate.

   (i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C.

   (ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C. Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C.



(c) S_2Cl_2 is a product of the reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.

Cl S S Cl

(ii) What is the approximate value of the Cl–S–S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl–S–S bond angles are not equal, include both angles.)

(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

(i) Identify all types of intermolecular forces present in $HCl(l)$.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 *M* $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

   (a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

   (b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

   (c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

   (d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

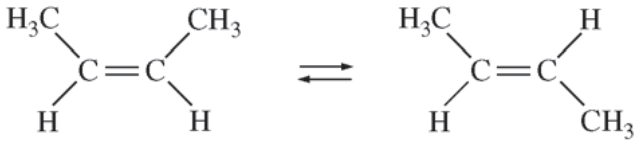
      (i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

      Enthalpy only Entropy only Both enthalpy and entropy

      (ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

   (e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.

   (f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 *M* $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.



cis-2-butene *trans*-2-butene

7. The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

STOP

END OF EXAM

AP CHEMISTRY • EXERCISE SHEET

5.6 Reading an Energy Profile

Name: _____ Class: _____ Date: _____ **Total: 11 marks**

KEY WORDS energy profile 能量图 • exothermic 放热 • endothermic 吸热 • transition state 过渡态 • activation energy 活化能

Objective

Build the skills to answer exam questions on **reading an energy profile** (reaction coordinate diagram).

You must be able to:

- read reactant and product energies and the **activation energy** E_a
- find ΔH from the diagram
- classify the reaction as **exothermic** 放热 or **endothermic** 吸热

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

The energy profile

The graph plots energy (y) against reaction progress (x): reactants on the left, a peak (the **transition state**), then products on the right.

Activation energy from the diagram

E_a is the height from the **reactants** up to the **peak**. A higher barrier means a slower reaction.

Enthalpy change

ΔH is the energy of **products minus reactants**:

- products **lower** than reactants $\rightarrow \Delta H < 0$, **exothermic** (releases energy);
- products **higher** $\rightarrow \Delta H > 0$, **endothermic**.

A worked reading

If reactants sit at 50 kJ, the peak at 120 kJ, and products at 30 kJ: $E_a = 120 - 50 = 70$ kJ; $\Delta H = 30 - 50 = -20$ kJ (exothermic).

2 Practice

Now apply the methods above.

2.1 On an energy profile, where is the activation energy measured from and to? [1]

2.2 Reactants at 60 kJ, products at 40 kJ. Find ΔH and classify it. [2]

2.3 What does the peak of an energy profile represent? [1]

3 Exam-style questions

3.1 An exothermic reaction has products that are [1]

- **A** higher in energy than reactants
- **B** lower in energy than reactants
- **C** equal to reactants
- **D** at the peak

3.2 An energy profile shows reactants at 80 kJ, the peak at 150 kJ, products at 110 kJ.

(a) Find the activation energy. [2]

(b) Find ΔH and state whether the reaction is exo- or endothermic. [2]

3.3 Sketch-describe how the energy profile changes when a catalyst is added, and state

which quantity is unaffected. [2]

Solutions

2.1 From the reactants up to the peak (transition state).

2.2 $\Delta H = 40 - 60 = -20$ kJ; exothermic.

2.3 The transition state (the highest-energy point).

3.1 B — products lower in energy than reactants.

3.2 (a) $E_a = 150 - 80 = 70$ kJ. (b) $\Delta H = 110 - 80 = +30$ kJ, endothermic.

3.3 A catalyst lowers the peak (a smaller E_a, an alternative pathway); ΔH (the reactant-to-product energy difference) is unchanged.

AP CHEMISTRY • EXERCISE SHEET

5.7 The Sequence of Steps

Name: _____ Class: _____ Date: _____ **Total: 9 marks**

KEY WORDS rate-determining step 决速步 • rate law 速率方程 • intermediates 中间体 • elementary steps 基元反应

Objective

Build the skills to answer exam questions on the **sequence of steps** — the rate-determining step.

You must be able to:

- identify the **rate-determining step** 决速步 (the slowest step)
- explain that the overall rate cannot exceed the slowest step
- check that steps add to the overall reaction

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The slowest step controls

A multi-step reaction goes no faster than its **slowest** step — the **rate-determining step (RDS)**. Like a slow lane on a highway, it sets the overall pace.

■ The bottleneck idea

If step 1 is slow and step 2 is fast, the overall rate is fixed by step 1. Speeding up the fast step does nothing; you must speed up the slow one.

■ The rate law comes from the RDS

The overall rate law is (usually) the rate law of the **rate-determining step**, written from its molecularity — provided that step's species are reactants (not intermediates).

■ Steps must sum correctly

Whatever the speeds, the elementary steps must add up (intermediates cancelling) to the overall balanced equation.

2 Practice

Now apply the methods above.

2.1 What is the rate-determining step? [1]

2.2 Step 1 is slow, step 2 is fast. Which sets the overall rate? [1]

2.3 If you speed up only the fast step, does the overall rate change much? [1]

3 Exam-style questions

3.1 The overall rate of a multi-step reaction is controlled by the [1]

- **A** fastest step
- **B** slowest step
- **C** first step always
- **D** last step always

3.2 A mechanism is: Step 1 (slow) $NO_2 + NO_2 \rightarrow NO_3 + NO$; Step 2 (fast) $NO_3 + CO \rightarrow NO_2 + CO_2$.

(a) Which step is rate-determining? [1]

(b) Write the rate law from that step. [2]

3.3 Explain, with the highway analogy or otherwise, why speeding up a fast step does not speed up the overall reaction if another step is slow. [2]

Solutions

2.1 The slowest step in the mechanism, which sets the overall rate.

2.2 Step 1 (the slow step).

2.3 No — it is limited by the slow step.

3.1 B — the slowest step.

3.2 (a) Step 1. (b) rate = $k[NO_2]^2$ (from the slow elementary step).

3.3 The overall reaction can only proceed as fast as its slowest bottleneck; a faster fast-step just waits on the slow step, so the total time barely changes.

AP CHEMISTRY • EXERCISE SHEET

5.8 Finding the Rate Law From a Mechanism

Name: _____ Class: _____ Date: _____ **Total: 9 marks**

KEY WORDS rate-determining step 决速步骤 • rate law 速率方程 • intermediates 中间体 • catalyst 催化剂

Objective

Build the skills to answer exam questions on **finding the rate law from a mechanism** (slow first step).

You must be able to:

- write the rate law from the **rate-determining step** when it is first
- confirm the mechanism is consistent with an experimental rate law
- avoid putting intermediates in the final rate law

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Slow first step → easy rate law

If the **first** step is the slow (rate-determining) step, its reactants are the original reactants, so the rate law comes straight from its molecularity.

■ A worked example

Mechanism: Step 1 (slow) $H_2 + ICl \rightarrow HI + HCl$; Step 2 (fast) $HI + ICl \rightarrow I_2 + HCl$. The slow step gives

$$\text{rate} = k[H_2][ICl].$$

■ Consistency check

A proposed mechanism is **valid** only if its predicted rate law matches the **experimental** one and its steps add to the overall equation.

■ No intermediates in the rate law

The final rate law may contain only **reactants** (or catalysts), never intermediates. If the slow step contains an intermediate, you must substitute for it (next subtopic).

2 Practice

Now apply the methods above.

2.1 If the slow step is $A + B \rightarrow X$, write the rate law. [1]

2.2 Can the final rate law contain an intermediate? [1]

2.3 A slow first step is $2NO \rightarrow N_2O_2$. Write its rate law. [1]

3 Exam-style questions

3.1 For a mechanism with a slow **first** step, the rate law is written from [1]

- **A** the overall equation
- **B** the slow first step's molecularity
- **C** the fast step
- **D** the products

3.2 A mechanism for $NO_2 + CO \rightarrow NO + CO_2$ is: Step 1 (slow) $NO_2 + NO_2 \rightarrow NO_3 + NO$; Step 2 (fast) $NO_3 + CO \rightarrow NO_2 + CO_2$.

(a) Write the predicted rate law. [2]

(b) The experimental rate law is rate $= k[NO_2]^2$. Is the mechanism consistent? [1]

3.3 Explain why the concentration of CO does **not** appear in the rate law for the mech-

anism in 3.2. [2]

Solutions

2.1 rate = k[A][B].

2.2 No.

2.3 rate = $k[\mathrm{NO}]^2$.

3.1 B — the slow first step's molecularity.

3.2 (a) rate = $k[\mathrm{NO_2}]^2$. (b) Yes — it matches the experimental rate law.

3.3 CO reacts only in the fast **second** step, after the rate-determining step; the slow step (which sets the rate) does not involve CO, so it is absent from the rate law.

. The following equation represents the decomposition of N_2O_5, for which the rate law is rate = $k[N_2O_5]$.

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

A sample of pure $N_2O_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $N_2O_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[N_2O_5](M)$
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

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

(b) The following mechanism is proposed for the decomposition of $N_2O_5(g)$.

Step 1: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$
Step 2: $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$
Step 3: $N_2O_5(g) + NO(g) \rightarrow 3\ NO_2(g)$

Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 5** on this page.

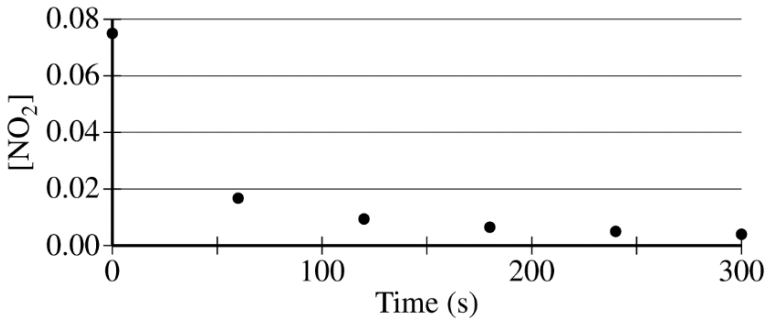
(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5, would the value of k increase, decrease, or remain the same? Explain your reasoning.

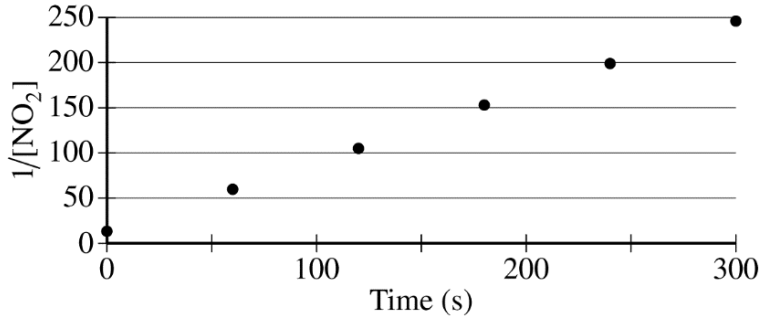
GO ON TO THE NEXT PAGE.

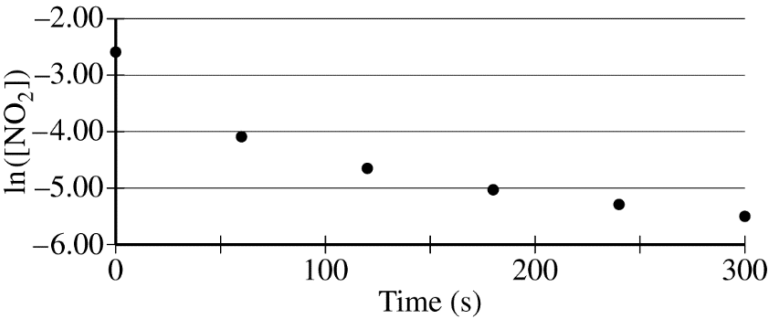
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ *slow*

Step 2: $NO_3(g) \rightarrow NO(g) + O_2(g)$ *fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

Step 1: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

Step 2: $N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$ *slow*

AP CHEMISTRY • EXERCISE SHEET

5.9 When the First Step Is Fast

Name: _____ Class: _____ Date: _____ **Total: 10 marks**

KEY WORDS intermediate 中间体 • rate law 速率方程 • activation energy 活化能 • rate-determining step 决速步骤

Objective

Build the skills to answer exam questions on mechanisms with a **fast first step** (a pre-equilibrium).

You must be able to:

- recognise when the slow step contains an **intermediate** 中间体
- substitute for the intermediate using the fast pre-equilibrium
- write a rate law with only reactants

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The problem

If the **first** step is fast and reversible and the **second** (slow) step uses an **intermediate**, the raw rate law would contain that intermediate — which is not allowed.

■ Pre-equilibrium substitution

The fast first step reaches equilibrium: forward rate = reverse rate. Solve that equality for the intermediate's concentration, then substitute it into the slow step's rate law.

■ A worked outline

Step 1 (fast) $2NO \rightleftharpoons N_2O_2$; Step 2 (slow) $N_2O_2 + O_2 \rightarrow 2NO_2$. Slow-step rate $= k[N_2O_2][O_2]$. From step 1's equilibrium, $[N_2O_2] \propto [NO]^2$, so

$$\text{rate} = k'[NO]^2[O_2].$$

■ The result

The final rate law has only reactants (NO and O_2) — the intermediate has been replaced.

2 Practice

Now apply the methods above.

2.1 Why can't an intermediate stay in the final rate law? [1]

2.2 In a fast equilibrium, the forward rate equals the _____ rate. [1]

2.3 If $[N_2O_2] \propto [NO]^2$, and rate $= k[N_2O_2][O_2]$, write the rate in terms of reactants. [2]

3 Exam-style questions

3.1 When the slow step contains an intermediate, you replace it using the [1]

- **A** overall equation
- **B** fast pre-equilibrium step
- **C** products
- **D** activation energy

3.2 Mechanism: Step 1 (fast) $A \rightleftharpoons B$ with $[B] \propto [A]$; Step 2 (slow) $B + C \rightarrow D$.

(a) Write the slow-step rate law. [1]

(b) Substitute for the intermediate to give the overall rate law. [2]

3.3 Explain why a fast reversible first step is called a "pre-equilibrium". [2]

Solutions

2.1 It is not a measurable starting reactant; the rate law must be in terms of reactants.

2.2 reverse (backward).

2.3 rate = $k[\mathrm{NO}]^2[\mathrm{O_2}]$.

3.1 B — the fast pre-equilibrium step.

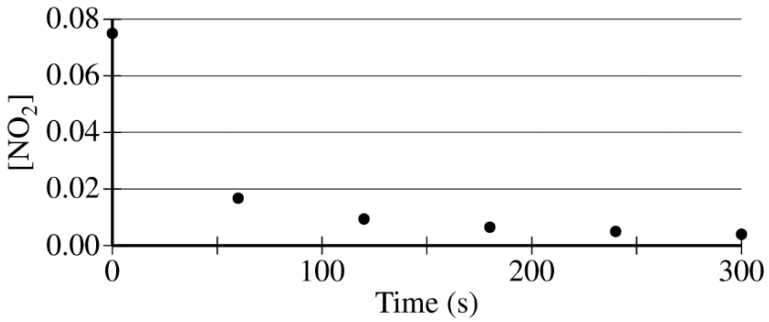
3.2 (a) rate = $k[\mathrm{B}][\mathrm{C}]$. (b) since $[\mathrm{B}] \propto [\mathrm{A}]$, rate = $k'[\mathrm{A}][\mathrm{C}]$.

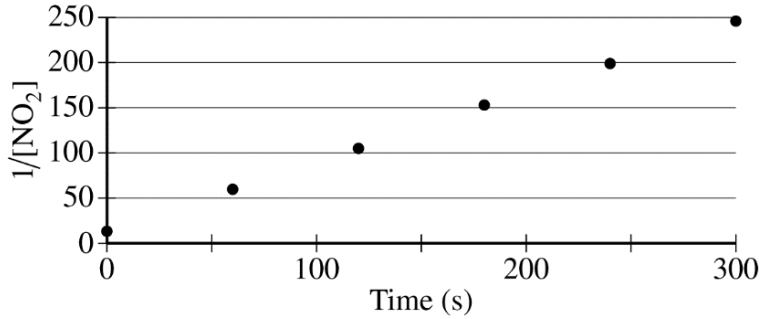
3.3 The fast reversible step reaches equilibrium **before** the slow step consumes its product, so an equilibrium is established ahead of the rate-determining step.

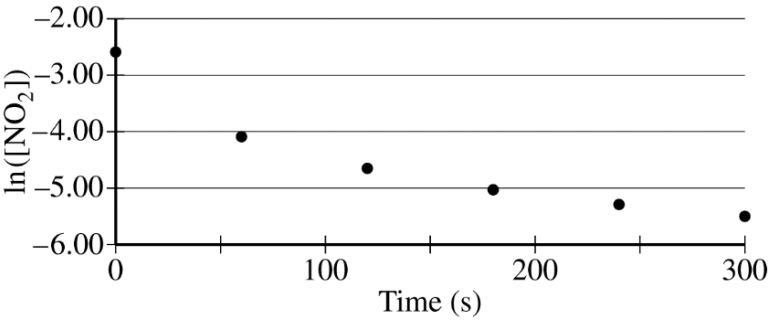
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ *slow*

Step 2: $NO_3(g) \rightarrow NO(g) + O_2(g)$ *fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

Step 1: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

Step 2: $N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$ *slow*

AP CHEMISTRY • EXERCISE SHEET

5.10 Energy Profiles for Many Steps

Name: _____ Class: _____ Date: _____ **Total: 10 marks**

KEY WORDS transition state 过渡态 • intermediates 中间体 • energy profile 能量图 • rate-determining step 决速步 • activation energy 活化能

Objective

Build the skills to answer exam questions on **energy profiles for multi-step reactions**.

You must be able to:

- read a profile with **two (or more) peaks**
- identify the **rate-determining step** as the highest peak
- locate **intermediates** in the valleys between peaks

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Many peaks = many steps

A multi-step reaction has **one peak per step**. Between two peaks sits a **valley** — a relatively stable **intermediate**.

■ The tallest barrier is rate-determining

The step with the **highest** peak (largest E_a measured from the valley/reactant before it) is the slowest — the **rate-determining step**.

■ Intermediates vs transition states

- **Peaks** are transition states (unstable, cannot be isolated).
- **Valleys** between peaks are intermediates (real species, briefly formed).

■ Overall ΔH

ΔH is still just **products minus reactants** (the start and end heights), regardless of how many peaks lie between.

2 Practice

Now apply the methods above.

2.1 How many steps does a profile with two peaks show? [1]

2.2 What does a valley between two peaks represent? [1]

2.3 Which step is rate-determining on a two-peak profile? [1]

3 Exam-style questions

3.1 On an energy profile, an intermediate is found at a [1]

- **A** peak
- **B** valley between peaks
- **C** the reactant position
- **D** the product position

3.2 A two-step profile: reactants at 40 kJ, peak 1 at 100 kJ, valley at 70 kJ, peak 2 at 90 kJ, products at 30 kJ.

(a) Find E_a for step 1 and for step 2 (each measured from the species before its peak). [2]

(b) Which step is rate-determining? [1]

(c) Find the overall ΔH. [1]

3.3 Explain the difference between a transition state and an intermediate on the profile.[2]

Solutions

2.1 Two steps.

2.2 An intermediate.

2.3 The step with the higher peak (larger activation energy).

3.1 B — a valley between peaks.

3.2 (a) step 1: $100 - 40 = 60$ kJ; step 2: $90 - 70 = 20$ kJ. (b) Step 1 (higher barrier). (c) $\Delta H = 30 - 40 = -10$ kJ.

3.3 A transition state (peak) is an unstable maximum that cannot be isolated; an intermediate (valley) is a real, briefly-stable species formed between steps.

AP CHEMISTRY • EXERCISE SHEET

5.11 How Catalysts Speed Things Up

Name: _____ Class: _____ Date: _____ **Total: 11 marks**

KEY WORDS catalyst 催化剂 • activation energy 活化能 • energy profile 能量图

Objective

Build the skills to answer exam questions on **catalysis** — how catalysts speed reactions.

You must be able to:

- explain that a **catalyst** 催化剂 provides a lower-E_a pathway
- state that a catalyst is **not consumed** and does not change ΔH
- distinguish **homogeneous** and **heterogeneous** catalysts

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

How a catalyst works

A **catalyst** provides an **alternative pathway** with a **lower activation energy**, so a larger fraction of collisions succeed and the reaction speeds up.

Not used up; ΔH unchanged

A catalyst is **regenerated** at the end (used in an early step, released in a later one), so it is not consumed. It lowers E_a but **does not change** ΔH — the reactant and product energies are the same.

Effect on both directions

Because it lowers the same barrier, a catalyst speeds up the **forward and reverse** reactions equally — it helps reach equilibrium faster, without shifting it.

Homogeneous vs heterogeneous

- **Homogeneous** — same phase as the reactants (e.g. an aqueous catalyst in solution).
- **Heterogeneous** — a different phase (e.g. a solid catalyst with gaseous reactants adsorbing on its surface).

2 Practice

Now apply the methods above.

2.1 How does a catalyst speed up a reaction? [1]

2.2 Does a catalyst change ΔH? [1]

2.3 Distinguish a homogeneous from a heterogeneous catalyst. [2]

3 Exam-style questions

3.1 A catalyst increases the rate by [1]

- **A** raising the temperature
- **B** providing a pathway with lower activation energy
- **C** increasing ΔH
- **D** removing products

3.2 On an energy profile, a catalyst is added.

(a) State what changes and what stays the same. [2]

(b) Explain why the catalyst is not consumed. [2]

3.3 Explain why a catalyst speeds up the forward and reverse reactions equally and

therefore does not shift the equilibrium position. [2]

Solutions

2.1 By providing an alternative pathway with a lower activation energy.

2.2 No.

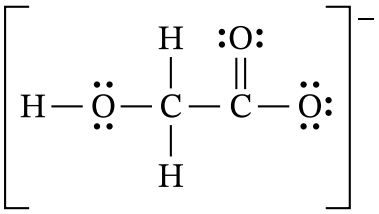
2.3 Homogeneous — same phase as the reactants; heterogeneous — a different phase (e.g. solid catalyst, gas reactants).

3.1 B — a lower-activation-energy pathway.

3.2 (a) The activation energy (peak) is lowered; ΔH (reactant and product energies) is unchanged. (b) It is used in an early step and regenerated in a later step, so it is not consumed overall.

3.3 The catalyst lowers the **same** barrier for both directions, so both the forward and reverse rates rise by the same factor; equilibrium (which depends on their ratio) is reached sooner but not shifted.

7. Answer the following questions about the glycolate ion, $C_2H_3O_3^-$, which acts as a base in aqueous solution. A Lewis diagram for the ion is provided.



A. On the Lewis diagram in part A, circle the atom that accepts the proton when the glycolate ion reacts with water.

When the glycolate ion reacts with water, it forms glycolic acid, $HC_2H_3O_3$, according to the following equation. The K_b expression for the reaction is provided.

$$C_2H_3O_3^-(aq) + H_2O(l) \rightleftarrows HC_2H_3O_3(aq) + OH^-(aq) \qquad K_b = \frac{[HC_2H_3O_3][OH^-]}{[C_2H_3O_3^-]}$$

B. At 25°C, a $2.5\ M$ solution of glycolate is found to have $[OH^-] = 1.3 \times 10^{-5}\ M$.

i. Calculate the value of K_b for the glycolate ion.

ii. Using your answer to part B (i), calculate the value of K_a for glycolic acid at 25°C.

Glycolic acid can be produced from the hydrolysis of methyl glycolate, $C_3H_6O_3$. A proposed mechanism for the reaction is given.

Step 1: $C_3H_6O_3 + H_3O^+ \rightleftarrows C_2H_5O_3^+ + CH_3OH$

Step 2: $\underline{C_2H_5O_3^+ + H_2O \rightleftarrows HC_2H_3O_3 + H_3O^+}$

Overall: $C_3H_6O_3 + H_2O \rightleftarrows HC_2H_3O_3 + CH_3OH$

C. A student claims that H_3O^+ is a catalyst for the reaction. Do you agree or disagree? Justify your answer based on the mechanism given.

STOP

END OF EXAM

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

$$\mathrm{HCOOH}(aq) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{HCOO^-}(aq) \qquad K_a = 1.8 \times 10^{-4}$$

1. Methanoic acid, HCOOH, ionizes according to the equation above.

   (a) Write the expression for the equilibrium constant, K_a, for the reaction.

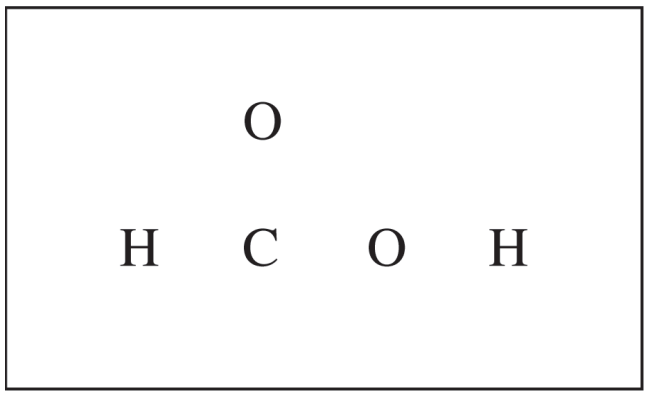
   (b) Calculate the pH of a 0.25 M solution of HCOOH.

GO ON TO THE NEXT PAGE.

Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

Continue your response to **QUESTION 1** on this page.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.



$$H_2NNH_2(aq) + H_2O(l) \rightleftarrows H_2NNH_3^+(aq) + OH^-(aq) \qquad K_b = 1.3 \times 10^{-6}$$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

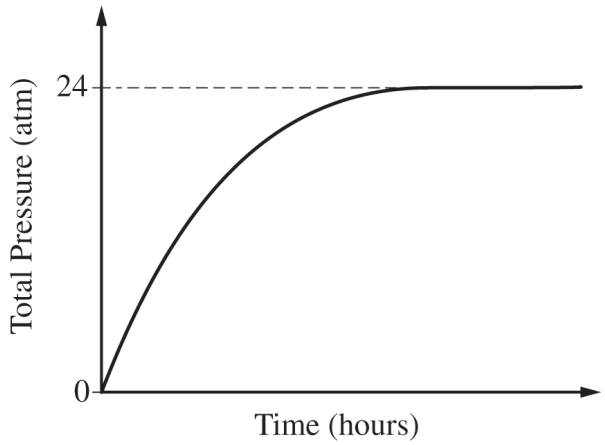
(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

GO ON TO THE NEXT PAGE.

When a catalyst is added to a solution of $HCOOH(aq)$, the reaction represented by the following equation occurs.

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$

(e) Is the reaction a redox reaction? Justify your answer.



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

GO ON TO THE NEXT PAGE.