$$H_{2(g)} + I_{2(g)} \rightarrow 2\ HI_{(g)}$$

For the exothermic reaction represented above, carried out at 298K, the rate law is as follows.

$$\text{Rate} = k[H_2][I_2]$$

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume

(b) Increase in volume of the reaction vessel at constant temperature

(c) Addition of catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.

(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

Answer the following questions related to the kinetics of chemical reactions.

$$I^-_{(aq)} + ClO^-_{(aq)} \xrightarrow{OH^-} IO^-_{(aq)} + Cl^-_{(aq)}$$

Iodide ion, I^-, is oxidized to hypoiodite ion, IO^-, by hypochlorite, ClO^-, in basic solution according to the equation above. Three initial-rate experiments were conducted; the results shown in the following table.

Experiment	$[I^-]$ (mol L^{-1})	$[ClO^-]$ (mol L^{-1})	Initial Rate of Formation of IO^- (mol L^{-1} s^{-1})
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

(i) $I^-_{(aq)}$

(ii) $ClO^-_{(aq)}$

(b) For the reaction,

(i) write the rate law that is consistent with the calculations in part (a);

(ii) calculate the value of the specific rate constant, k, and specify units.

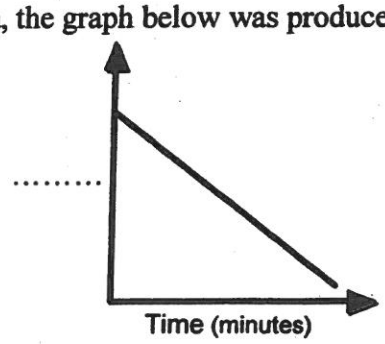
The catalyzed decomposition of hydrogen peroxide, $H_2O_{2(aq)}$, is represented by the following equation.

$$2\ H_2O_{2(aq)} \xrightarrow{catalyst} 2\ H_2O_{(l)} + O_{2(g)}$$

The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below.

$[H_2O_2]$ (mol L^{-1})	Time (minutes)
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced.



(i) Label the vertical axis of the graph

(ii) What are the units of the rate constant, k, for the decomposition of $H_2O_{2(aq)}$?

(iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 *M* $H_2O_{2(aq)}$

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

A rate study of the reaction yielded the data recorded in the table below.

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

(i) NO

(ii) O_2

(e) Write the expression for the rate law for the reaction as determined from the experimental data.

(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

STOP

If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.

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$$8\ H^+(aq) + 4\ Cl^-(aq) + MnO_4^-(aq) \rightarrow 2\ Cl_2(g) + Mn^{3+}(aq) + 4\ H_2O(l)$$

3. $Cl_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

(a) A 25.00 mL sample of 0.250 *M* NaCl reacts completely with excess $KMnO_4(aq)$. The $Cl_2(g)$ produced is dried and stored in a sealed container. At 22°C the pressure of the $Cl_2(g)$ in the container is 0.950 atm.

(i) Calculate the number of moles of $Cl^-(aq)$ present before any reaction occurs.

(ii) Calculate the volume, in L, of the $Cl_2(g)$ in the sealed container.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of Disappearance of MnO_4^- in $M\ s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

(b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.

(i) Cl^-

(ii) MnO_4^-

(c) The reaction is known to be third order with respect to H^+. Using this information and your answers to part (b) above, complete both of the following:

(i) Write the rate law for the reaction.

(ii) Calculate the value of the rate constant, k, for the reaction, including appropriate units.

X (d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

STOP

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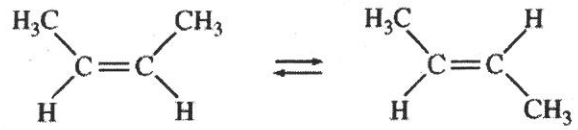

cis-2-butene *trans*-2-butene

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.

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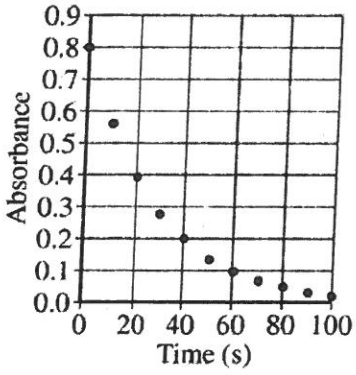
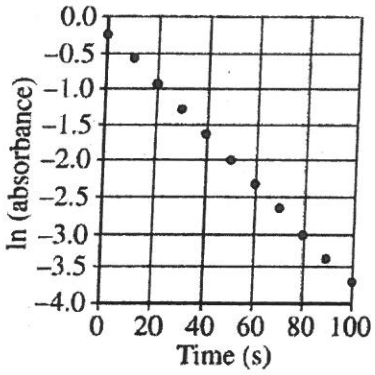
$$Na_2C_{37}H_{34}N_2S_3O_9 + OCl^- \rightarrow \text{products}$$

blue *colorless*

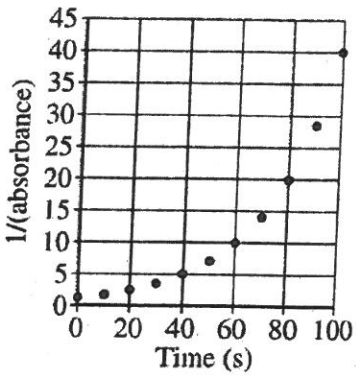
5. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the 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?

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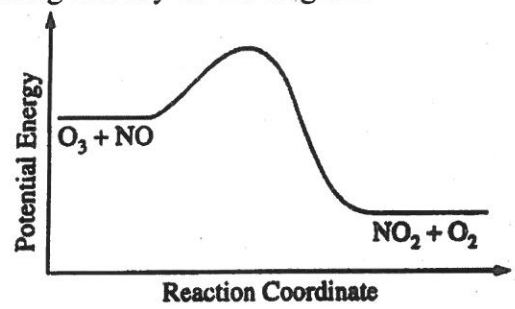
Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram.

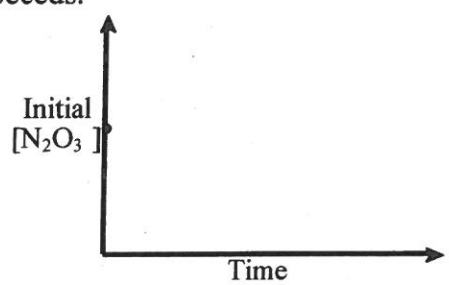


(i) The activation energy *(E_a)* for the forward reaction

(ii) The enthalpy change (ΔH) for the reaction

(b) The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.

(i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

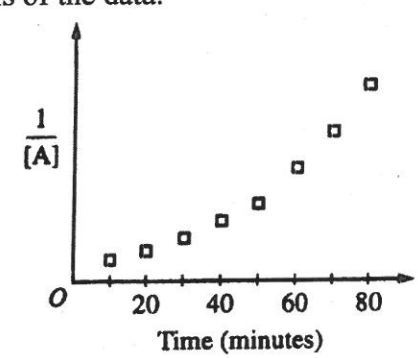


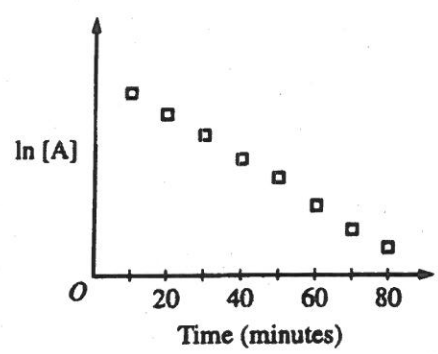
(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, *t*.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, *k*, could be determined.

(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, *k*? Explain.

(c) Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.





Use the information in the graphs above to answer the following.

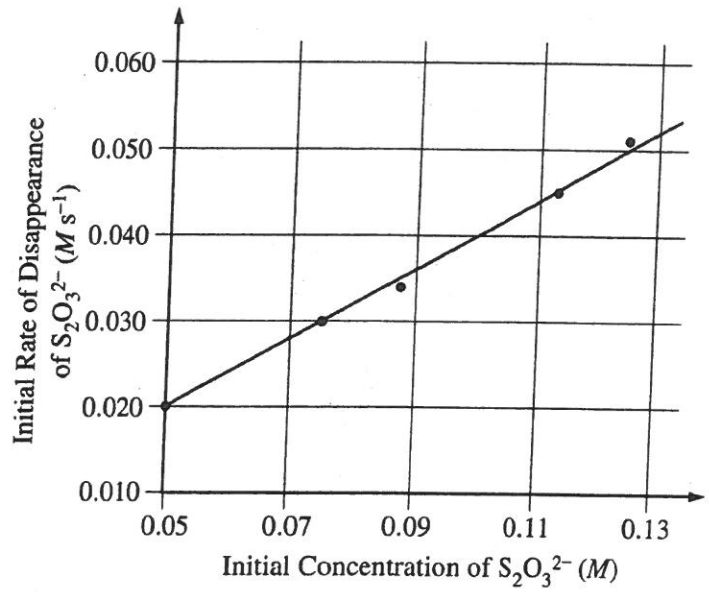
(i) Write the rate-law expression for the reaction. Justify your answer.

(ii) Describe how to determine the value of the rate constant for the reaction.

$$S_2O_3^{2-}(aq) \xrightarrow{H^+} SO_3^{2-}(aq) + S(s)$$

2. A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $S_2O_3^{2-}$ (aq) (M)	Initial Rate of Disappearance of $S_2O_3^{2-}$ (aq) $(M\ s^{-1})$
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



(a) Identify the independent variable in the experiment.

(b) Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.

(c) Determine the value of the rate constant, k, for the reaction. Include units in your answer. Show how you arrived at your answer.

(d) In another trial the student mixed 0.10 M $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 M.

(e) On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

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6. In an experiment, all the air in a rigid 2.0 L flask is pumped out. Then some liquid ethanol is injected into the sealed flask, which is held at 35°C. The amount of liquid ethanol initially decreases, but after five minutes the amount of liquid ethanol in the flask remains constant. Ethanol has a boiling point of 78.5°C and an equilibrium vapor pressure of 100 torr at 35°C.

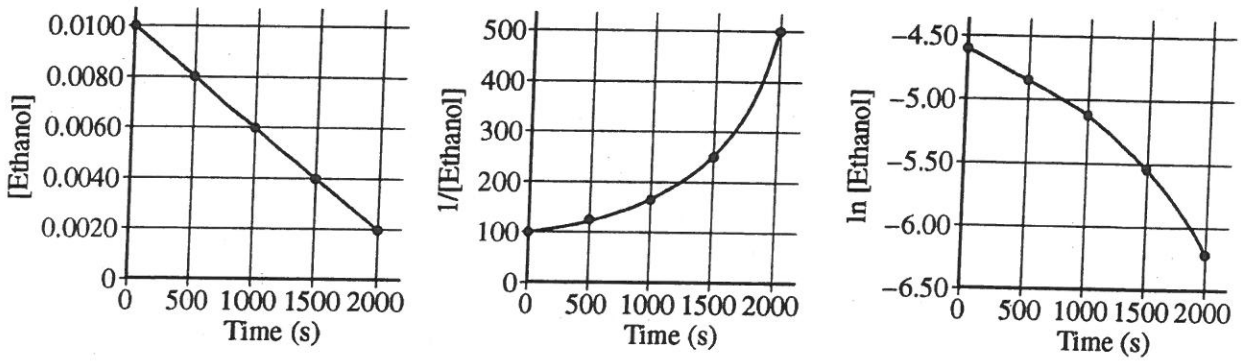
   (a) When the amount of liquid ethanol in the flask is constant, is the pressure in the flask greater than, less than, or equal to 100 torr? Justify your answer.

   (b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 *M*. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

The concentration of ethanol gas over time is used to create the three graphs below.



   (c) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

      (i) Determine the order of the reaction with respect to ethanol. Justify your answer.

      (ii) Write the rate law for the reaction.

      (iii) Determine the rate constant for the reaction, including units.

   (d) The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

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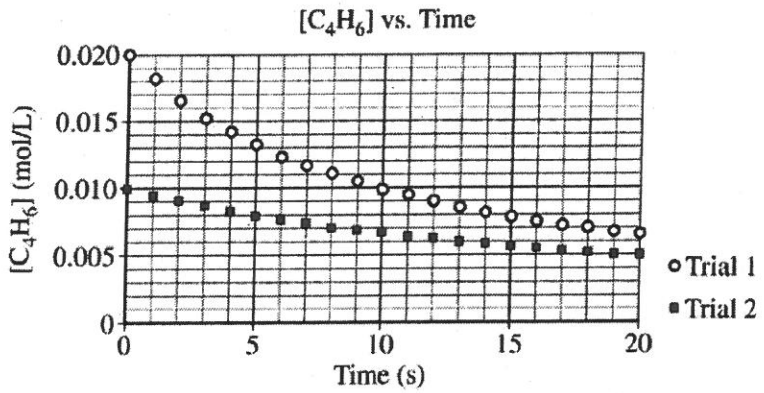
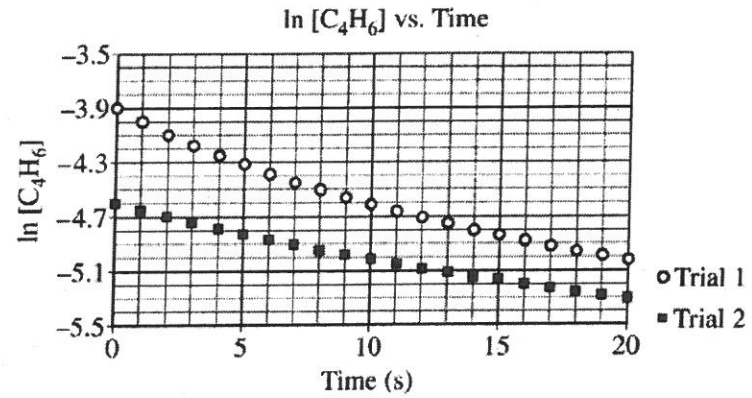
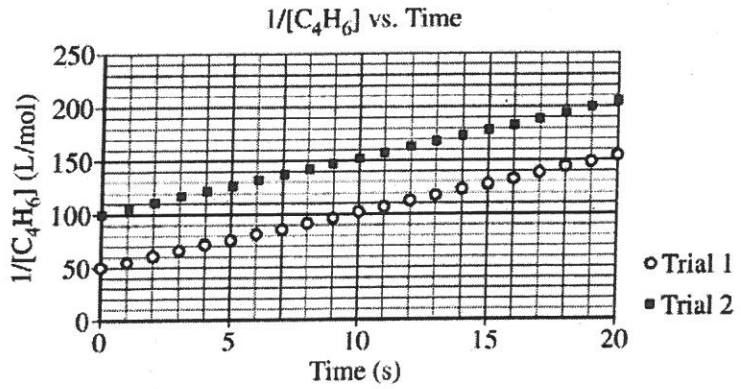
$$2\,C_4H_6(g) \rightarrow C_8H_{12}(g)$$

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.







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(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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