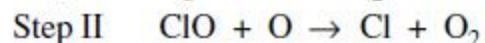
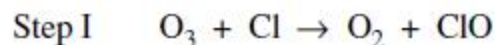


2002.7 – Mechanisms  
2003B.8 – Half Life  
2004.3 – Beer, IRL, Half Life  
2004B.3 – Mole, Half Life  
2005.3 – Differential, catalyst  
2005B.3 – Mole, IRL  
2006.6 – IMF, Catalyst  
2008B.2 – Differential, Mechanisms  
2009.3 – Stoich, bond energy,  $E=h\nu/c=\lambda\nu$ , Mechanisms  
2009B.2 – Differential, IRL  
2010.3 – IGL, Differential  
2010B.6 – Differential, Mechanisms  
2011.6 – KMT, IRL  
2013A.5 – Collision Theory/KMT, Mechanisms, PE Diagram  
2013B.3 – Differential, Mechanisms  
2013C.4 – Collision Theory, Mechanisms  
2014.7 – Differential (No math), Half life, KE  
2015.5 – IRL (Graph), Factors, Beers  
2016.5 – IGL, IRL (Graph), IRL  
2016B.3 – Ch3, IGL, Lab (Rate)  
2016B.7 – MVMV, Lab procedures, Beers  
2017B.3 – VSEPR (Resonance), Bond Energy, Half life  
2018.7 – PES, Half Life  
2018B.1 – VSEPR, bond angle,  $e^-$  config, PES, Differential, Lab  
2018B.4 – Beers, Mole, Mass %

An environmental concern is the depletion of  $\text{O}_3$  in Earth's upper atmosphere, where  $\text{O}_3$  is normally in equilibrium with  $\text{O}_2$  and  $\text{O}$ . A proposed mechanism for the depletion of  $\text{O}_3$  in the upper atmosphere is shown below.



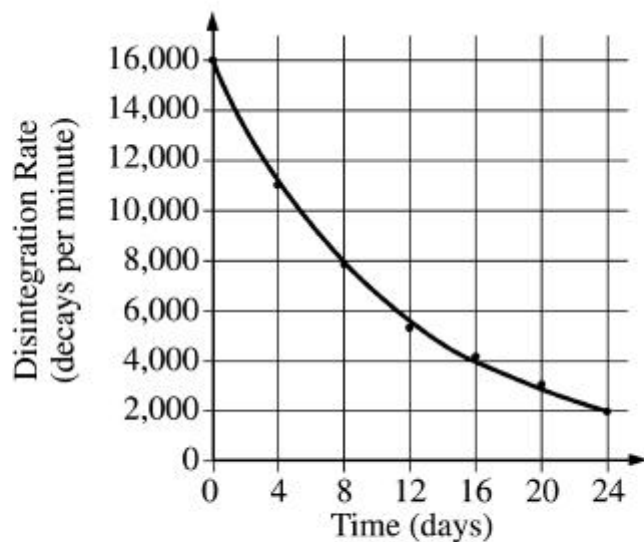
- (a) Write a balanced equation for the overall reaction represented by Step I and Step II above.
- (b) Clearly identify the catalyst in the mechanism above. Justify your answer.
- (c) Clearly identify the intermediate in the mechanism above. Justify your answer.
- (d) If the rate law for the overall reaction is found to be  $\text{rate} = k[\text{O}_3][\text{Cl}]$ , determine the following.
  - (i) The overall order of the reaction
  - (ii) Appropriate units for the rate constant,  $k$
  - (iii) The rate-determining step of the reaction, along with justification for your answer

The decay of the radioisotope I-131 was studied in a laboratory. I-131 is known to decay by beta ( ${}_{-1}^0e$ ) emission

(a) **REMOVED**

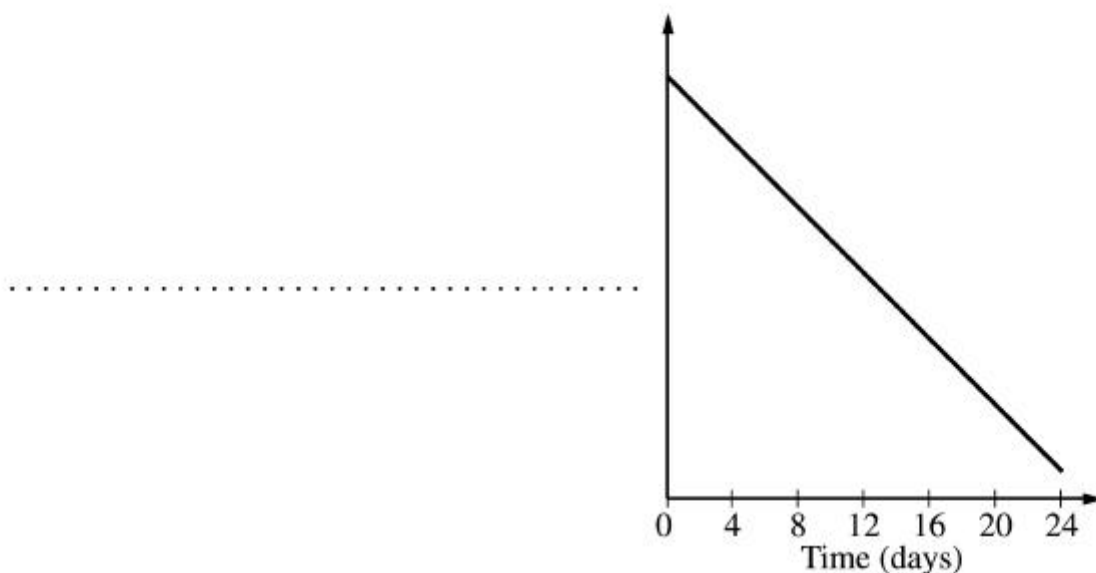
(b) **REMOVED**

The radioactivity of a sample of I-131 was measured. The data collected are plotted on the graph below.



(c) Determine the half-life,  $t_{1/2}$ , of I-131 using the graph above.

(d) The data can be used to show that the decay of I-131 is a first-order reaction, as indicated on the graph below.



(i) Label the vertical axis of the graph above.

(ii) What are the units of the rate constant,  $k$ , for the decay reaction?

(iii) Explain how the half-life of I-131 can be calculated using the slope of the line plotted on the graph.

(e) Compare the value of the half-life of I-131 at 25°C to its value at 50°C.

The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of  $5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$  and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

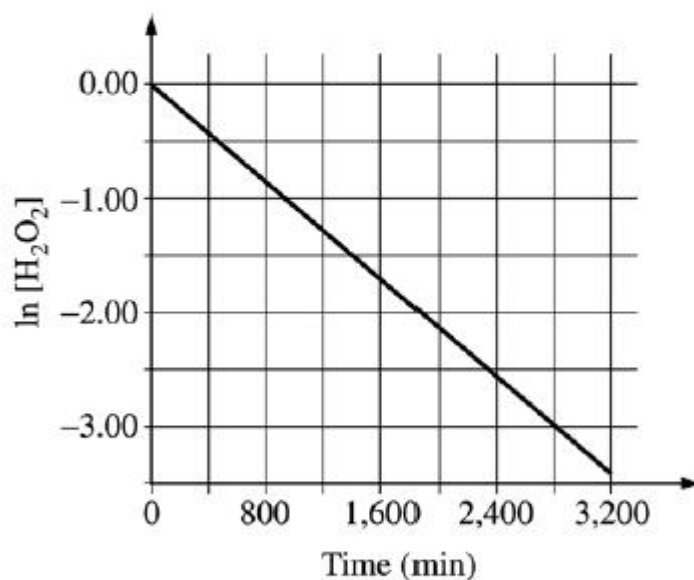
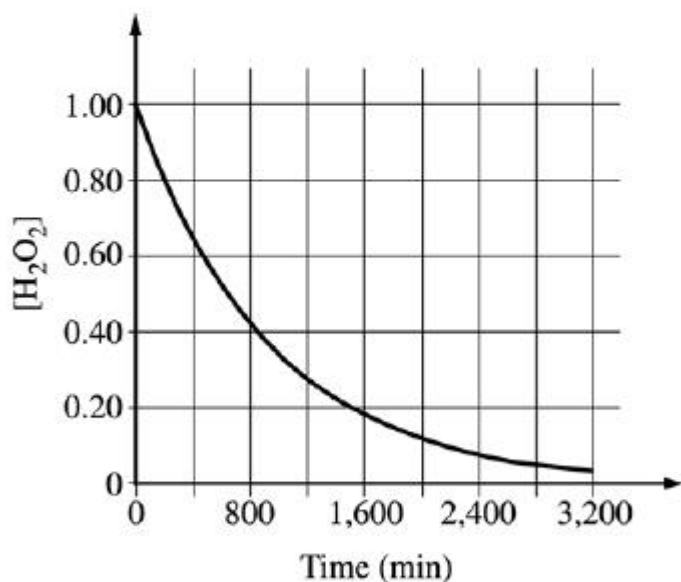
[X] (M)	Absorbance	Time (min)
?	0.600	0.0
$4.00 \times 10^{-5}$	0.200	35.0
$3.00 \times 10^{-5}$	0.150	44.2
$1.50 \times 10^{-5}$	0.075	?

- (a) Calculate the initial concentration of the colored species.
- (b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
- (c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
- (d) Calculate the half-life of the reaction. Include units with your answer.
- (e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where  $T$  is temperature. This graph can be used to determine the activation energy,  $E_a$ , of the reaction.
- (i) **REMOVED**
- (ii) **REMOVED**



Hydrogen peroxide decomposes according to the equation above.

- (a) An aqueous solution of  $\text{H}_2\text{O}_2$  that is 6.00 percent  $\text{H}_2\text{O}_2$  by mass has a density of  $1.03 \text{ g mL}^{-1}$ . Calculate each of the following.
- The original number of moles of  $\text{H}_2\text{O}_2$  in a 125 mL sample of the 6.00 percent  $\text{H}_2\text{O}_2$  solution
  - The number of moles of  $\text{O}_2(g)$  that are produced when all of the  $\text{H}_2\text{O}_2$  in the 125 mL sample decomposes
- (b) The graphs below show results from a study of the decomposition of  $\text{H}_2\text{O}_2$ .



- Write the rate law for the reaction. Justify your answer.
- Determine the half-life of the reaction.
- Calculate the value of the rate constant,  $k$ . Include appropriate units in your answer.
- Determine  $[\text{H}_2\text{O}_2]$  after 2,000 minutes elapse from the time the reaction began.



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



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

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

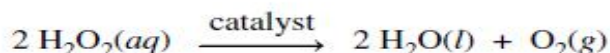
(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

- (i)  $\text{I}^{-}(\text{aq})$
- (ii)  $\text{ClO}^{-}(\text{aq})$

(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.

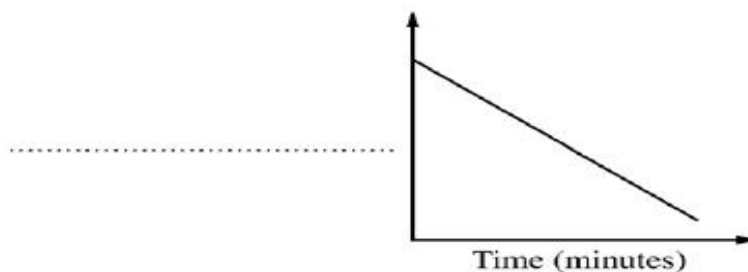
The catalyzed decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2(\text{aq})$ , is represented by the following equation.



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.

$[\text{H}_2\text{O}_2]$ (mol L <sup>-1</sup> )	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.

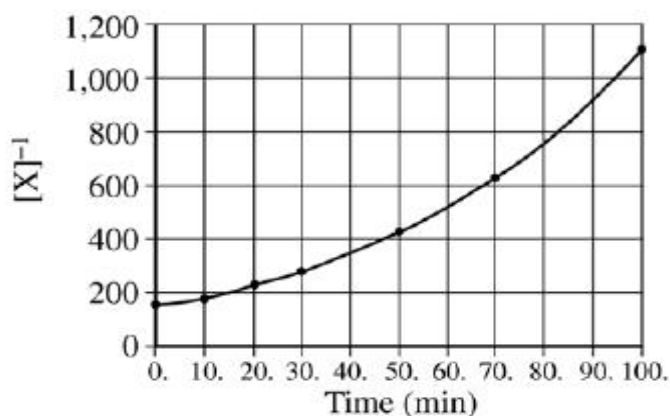
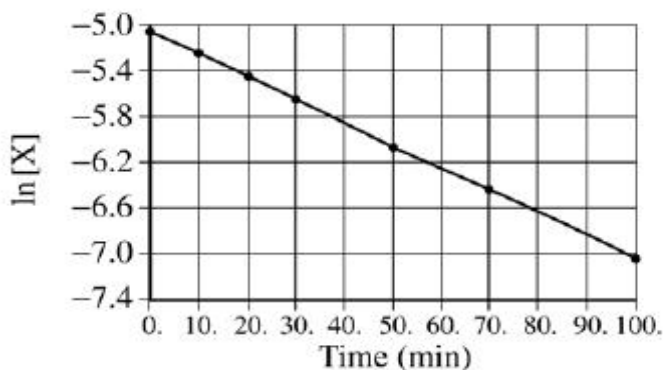
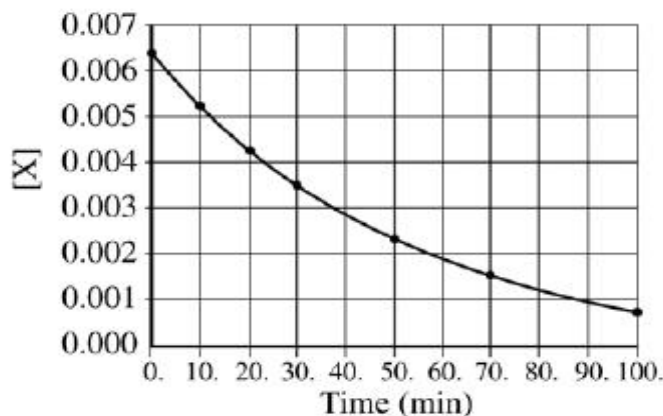


- (i) Label the vertical axis of the graph.
- (ii) What are the units of the rate constant,  $k$ , for the decomposition of  $\text{H}_2\text{O}_2(\text{aq})$ ?
- (iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M  $\text{H}_2\text{O}_2(\text{aq})$ .



The decomposition of gas X to produce gases Y and Z is represented by the equation above. In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from this experiment were used to produce the information in the table below, which is plotted in the graphs that follow.

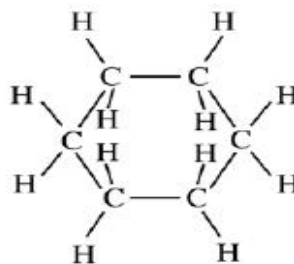
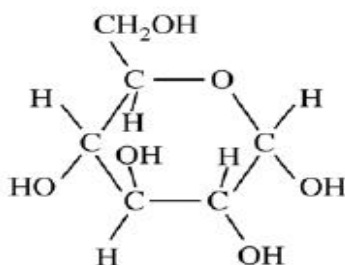
Time (minutes)	[X] (mol L <sup>-1</sup> )	ln [X]	[X] <sup>-1</sup> (L mol <sup>-1</sup> )
0	0.00633	-5.062	158
10.	0.00520	-5.259	192
20.	0.00427	-5.456	234
30.	0.00349	-5.658	287
50.	0.00236	-6.049	424
70.	0.00160	-6.438	625
100.	0.000900	-7.013	1,110



- How many moles of X were initially in the flask?
- How many molecules of Y were produced in the first 20. minutes of the reaction?
- What is the order of this reaction with respect to X? Justify your answer.
- Write the rate law for this reaction.
- Calculate the specific rate constant for this reaction. Specify units.
- Calculate the concentration of X in the flask after a total of 150. minutes of reaction.

Answer each of the following in terms of principles of molecular behavior and chemical concepts.

- (a) The structures for glucose,  $C_6H_{12}O_6$ , and cyclohexane,  $C_6H_{12}$ , are shown below.

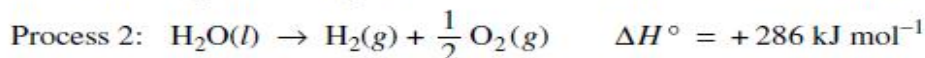


Identify the type(s) of intermolecular attractive forces in

- (i) pure glucose
- (ii) pure cyclohexane

- (b) Glucose is soluble in water but cyclohexane is not soluble in water. Explain.

- (c) Consider the two processes represented below.



- (i) For each of the two processes, identify the type(s) of intermolecular or intramolecular attractive forces that must be overcome for the process to occur.
- (ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

When water boils,  $H_2O$  molecules break apart to form hydrogen molecules and oxygen molecules.

- (d) Consider the four reaction-energy profile diagrams shown below.

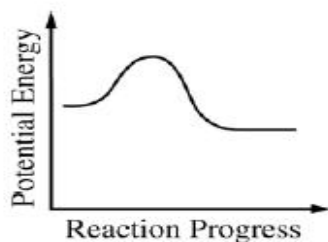


Diagram 1

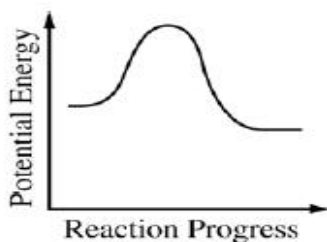


Diagram 2

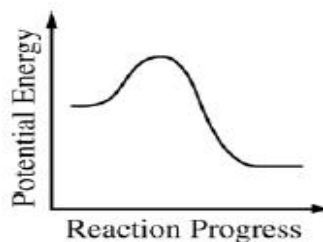


Diagram 3

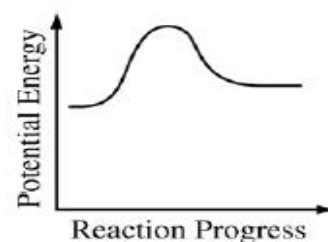
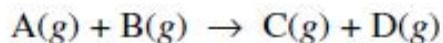


Diagram 4

- (i) Identify the two diagrams that could represent a catalyzed and an uncatalyzed reaction pathway for the same reaction. Indicate which of the two diagrams represents the catalyzed reaction pathway for the reaction.
- (ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

Adding a catalyst to a reaction mixture adds energy that causes the reaction to proceed more quickly.

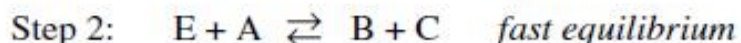
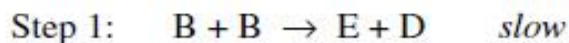




For the gas-phase reaction represented above, the following experimental data were obtained.

Experiment	Initial [A] (mol L <sup>-1</sup> )	Initial [B] (mol L <sup>-1</sup> )	Initial Reaction Rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.033	0.034	$6.67 \times 10^{-4}$
2	0.034	0.137	$1.08 \times 10^{-2}$
3	0.136	0.136	$1.07 \times 10^{-2}$
4	0.202	0.233	?

- Determine the order of the reaction with respect to reactant A . Justify your answer.
- Determine the order of the reaction with respect to reactant B . Justify your answer.
- Write the rate law for the overall reaction.
- Determine the value of the rate constant,  $k$  , for the reaction. Include units with your answer.
- Calculate the initial reaction rate for experiment 4.
- The following mechanism has been proposed for the reaction.



Provide two reasons why the mechanism is acceptable.

- In the mechanism in part (f), is species E a catalyst, or is it an intermediate? Justify your answer.



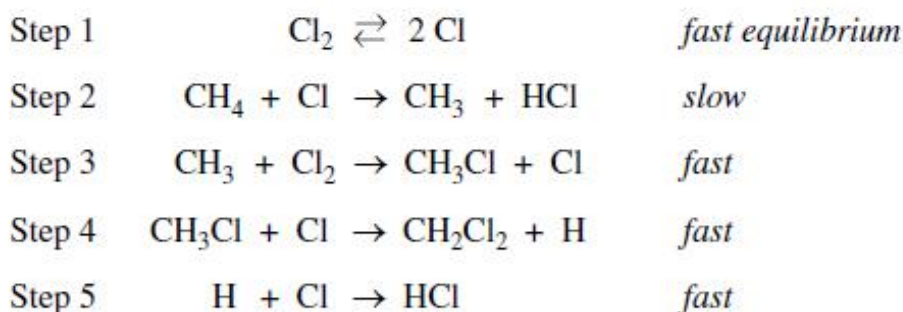
Methane gas reacts with chlorine gas to form dichloromethane and hydrogen chloride, as represented by the equation above.

- (a) A 25.0 g sample of methane gas is placed in a reaction vessel containing 2.58 mol of  $\text{Cl}_2(\text{g})$ .
- Identify the limiting reactant when the methane and chlorine gases are combined. Justify your answer with a calculation.
  - Calculate the total number of moles of  $\text{CH}_2\text{Cl}_2(\text{g})$  in the container after the limiting reactant has been totally consumed.

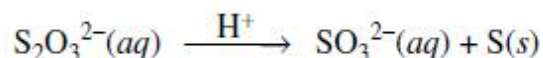
Initiating most reactions involving chlorine gas involves breaking the Cl–Cl bond, which has a bond energy of  $242 \text{ kJ mol}^{-1}$ .

- Calculate the amount of energy, in joules, needed to break a single Cl–Cl bond.
- Calculate the longest wavelength of light, in meters, that can supply the energy per photon necessary to break the Cl–Cl bond.

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.

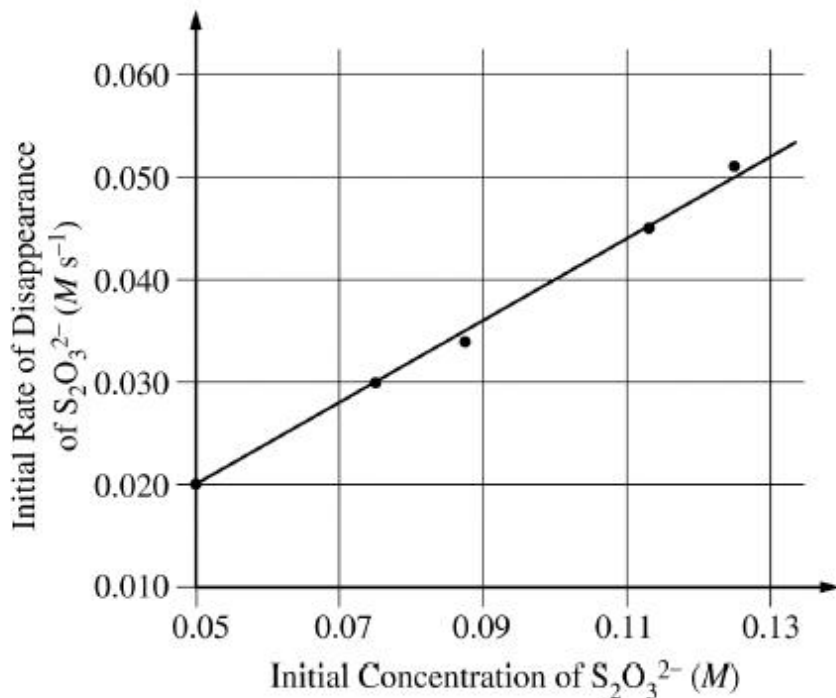


- In the mechanism, is  $\text{CH}_3\text{Cl}$  a catalyst, or is it an intermediate? Justify your answer.
- Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.
  - $\text{CH}_4(\text{g})$
  - $\text{Cl}_2(\text{g})$



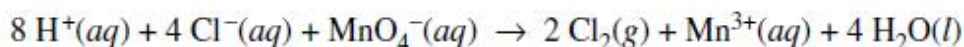
A student performed an experiment to investigate the decomposition of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of  $\text{S}_2\text{O}_3^{2-}(\text{aq})$ . 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 $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (M)	Initial Rate of Disappearance of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ ( $\text{M s}^{-1}$ )
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



- Identify the independent variable in the experiment.
- Determine the order of the reaction with respect to  $\text{S}_2\text{O}_3^{2-}$ . Justify your answer by using the information above.
- Determine the value of the rate constant,  $k$ , for the reaction. Include units in your answer. Show how you arrived at your answer.
- In another trial the student mixed  $0.10 \text{ M}$   $\text{Na}_2\text{S}_2\text{O}_3$  with hydrochloric acid. Calculate the amount of time it would take for the concentration of  $\text{S}_2\text{O}_3^{2-}$  to drop to  $0.020 \text{ M}$ .
- 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.





$\text{Cl}_2(g)$  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.

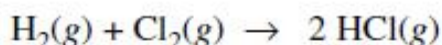
- (a) A 25.00 mL sample of 0.250 M NaCl reacts completely with excess  $\text{KMnO}_4(aq)$ . The  $\text{Cl}_2(g)$  produced is dried and stored in a sealed container. At 22°C the pressure of the  $\text{Cl}_2(g)$  in the container is 0.950 atm.
- Calculate the number of moles of  $\text{Cl}^-(aq)$  present before any reaction occurs.
  - Calculate the volume, in L, of the  $\text{Cl}_2(g)$  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	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of Disappearance of $\text{MnO}_4^-$ in $M \text{ s}^{-1}$
1	0.0104	0.00400	3.00	$2.25 \times 10^{-8}$
2	0.0312	0.00400	3.00	$2.03 \times 10^{-7}$
3	0.0312	0.00200	3.00	$1.02 \times 10^{-7}$

- (b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.
- $\text{Cl}^-$
  - $\text{MnO}_4^-$
- (c) The reaction is known to be third order with respect to  $\text{H}^+$ . Using this information and your answers to part (b) above, complete both of the following:
- Write the rate law for the reaction.
  - Calculate the value of the rate constant,  $k$ , for the reaction, including appropriate units.
- (d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.



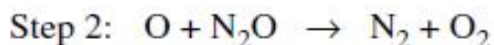
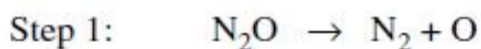


The table below gives data for a reaction rate study of the reaction represented above.

Experiment	Initial $[\text{H}_2]$ (mol L <sup>-1</sup> )	Initial $[\text{Cl}_2]$ (mol L <sup>-1</sup> )	Initial Rate of Formation of HCl (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.00100	0.000500	$1.82 \times 10^{-12}$
2	0.00200	0.000500	$3.64 \times 10^{-12}$
3	0.00200	0.000250	$1.82 \times 10^{-12}$

- Determine the order of the reaction with respect to  $\text{H}_2$  and justify your answer.
- Determine the order of the reaction with respect to  $\text{Cl}_2$  and justify your answer.
- Write the overall rate law for the reaction.
- Write the units of the rate constant.
- Predict the initial rate of the reaction if the initial concentration of  $\text{H}_2$  is 0.00300 mol L<sup>-1</sup> and the initial concentration of  $\text{Cl}_2$  is 0.000500 mol L<sup>-1</sup>.

The gas-phase decomposition of nitrous oxide has the following two-step mechanism.



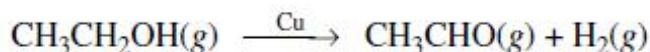
- Write the balanced equation for the overall reaction.
- Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.
- Identify the slower step in the mechanism if the rate law for the reaction was determined to be  $\text{rate} = k [\text{N}_2\text{O}]$ . Justify your answer.

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.

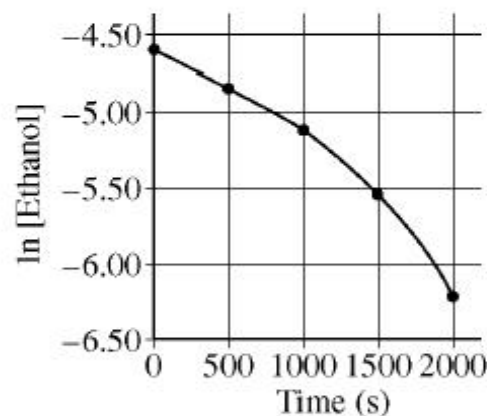
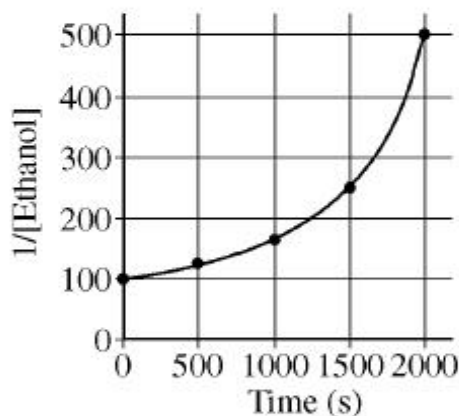
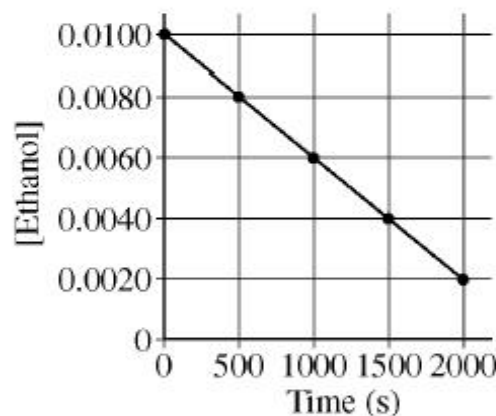
(a) **REMOVED**

(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.



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.

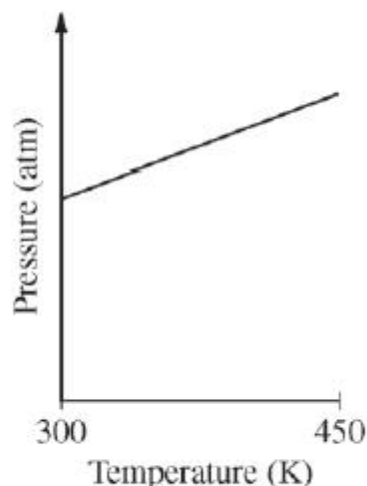
(i) Determine the order of the reaction with respect to ethanol. Justify your answer.

(ii) Write the rate law for the reaction.

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

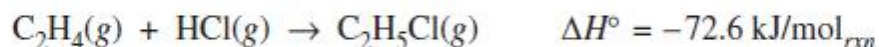
(d) The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

A sample of  $\text{C}_2\text{H}_4(\text{g})$  is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



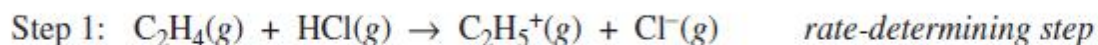
- (a) Describe TWO reasons why the pressure changes as the temperature of the  $\text{C}_2\text{H}_4(\text{g})$  increases. Your descriptions must be in terms of what occurs at the molecular level.

$\text{C}_2\text{H}_4(\text{g})$  reacts readily with  $\text{HCl}(\text{g})$  to produce  $\text{C}_2\text{H}_5\text{Cl}(\text{g})$ , as represented by the following equation.



- (b) When  $\text{HCl}(\text{g})$  is injected into the container of  $\text{C}_2\text{H}_4(\text{g})$  at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

It is proposed that the formation of  $\text{C}_2\text{H}_5\text{Cl}(\text{g})$  proceeds via the following two-step reaction mechanism.



- (c) Write the rate law for the reaction that is consistent with the reaction mechanism above.
- (d) Identify an intermediate in the reaction mechanism above.





$\text{NO}(g)$  reacts with  $\text{Br}_2(g)$ , as represented by the equation above. An experiment was performed to study the rate of the reaction at 546 K. Data from three trials are shown in the table below.

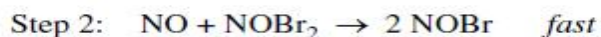
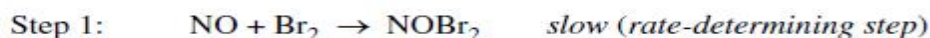
Trial	Initial $[\text{NO}]$ ( $M$ )	Initial $[\text{Br}_2]$ ( $M$ )	Initial Rate of Consumption of $\text{Br}_2$ ( $M \text{ s}^{-1}$ )
1	0.10	0.20	12.0
2	0.40	0.20	192.0
3	0.10	0.60	36.0

- (a) Using the data in the table, determine the order of the reaction with respect to each of the following reactants. In each case, justify your answer.
- $\text{Br}_2$
  - $\text{NO}$
- (b) Write the rate law for the reaction.
- (c) Determine the value of the rate constant,  $k$ , for the reaction. Include units with your answer.

Question #3-d did not align with the new course and has been removed.

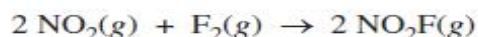
- (e) At a later time during trial 2, the concentration of  $\text{Br}_2(g)$  is determined to be  $0.16 M$ .
- Determine the concentration of  $\text{NO}(g)$  at that time.
  - Calculate the rate of consumption of  $\text{Br}_2(g)$  at that time.

A proposed two-step mechanism for the reaction is represented below.



- (f) Is the proposed mechanism consistent with the rate law determined in part (b) ? Justify your answer.





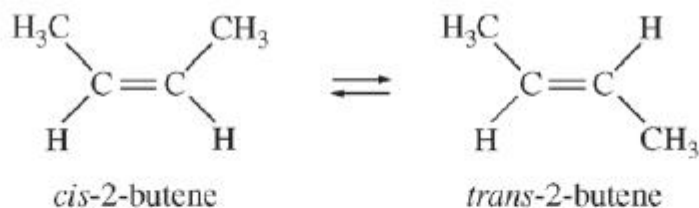
It is proposed that the reaction represented above proceeds via the mechanism represented by the two elementary steps shown below.



- (a) Step I of the proposed mechanism involves the collision between  $\text{NO}_2$  and  $\text{F}_2$  molecules. This step is slow even though such collisions occur very frequently in a mixture of  $\text{NO}_2(g)$  and  $\text{F}_2(g)$ . Consider a specific collision between a molecule of  $\text{NO}_2$  and a molecule of  $\text{F}_2$ .
- (i) One factor that affects whether the collision will result in a reaction is the magnitude of the collision energy. Explain.
  - (ii) Identify and explain one other factor that affects whether the collision will result in a reaction.
- (b) Consider the following potential rate laws for the reaction. Circle the rate law below that is consistent with the mechanism proposed above. Explain the reasoning behind your choice in terms of the details of the elementary steps of the mechanism.

$$\text{rate} = k[\text{NO}_2]^2[\text{F}_2]$$

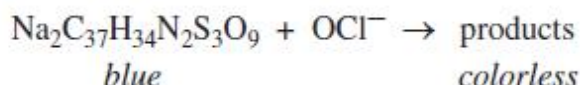
$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$



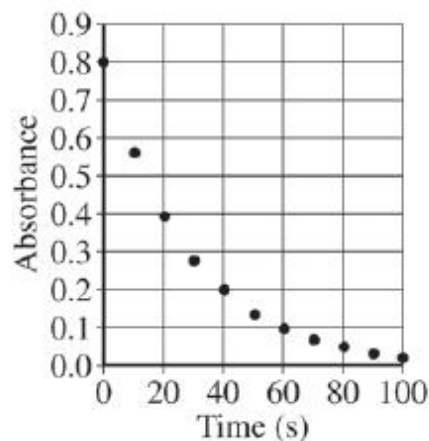
The half-life ( $t_{1/2}$ ) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{\text{cis-2-butene}}$ (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.

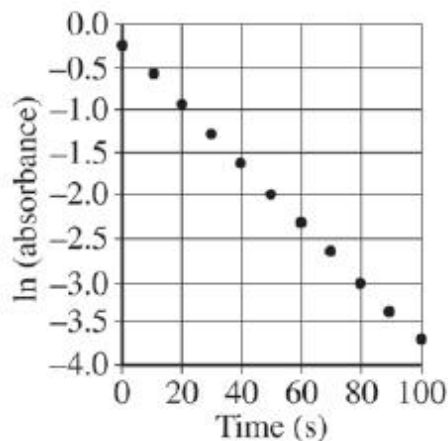
- The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.
- Calculate the rate constant,  $k$ , for the reaction at 350. K. Include appropriate units with your answer.
- Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.
- 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.



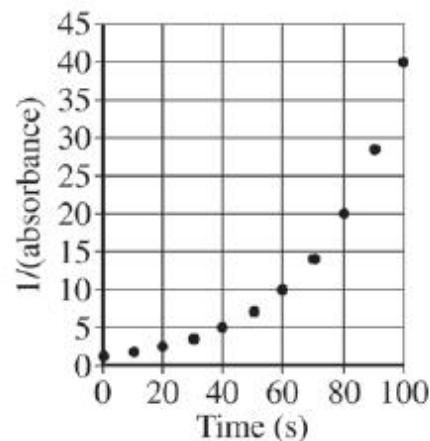
Blue food coloring can be oxidized by household bleach (which contains  $\text{OCl}^-$ ) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process.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



Graph I



Graph II



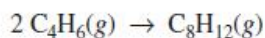
Graph III

- (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

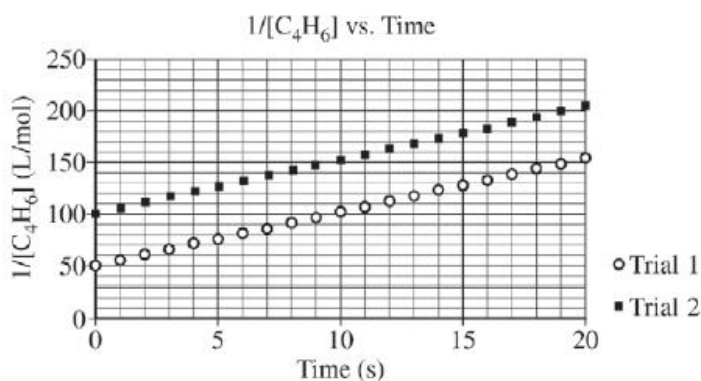
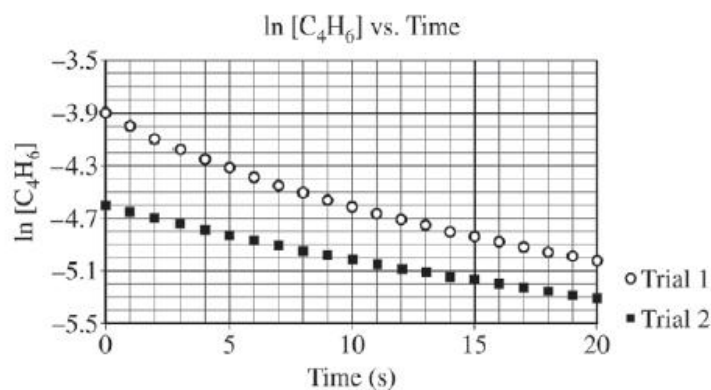
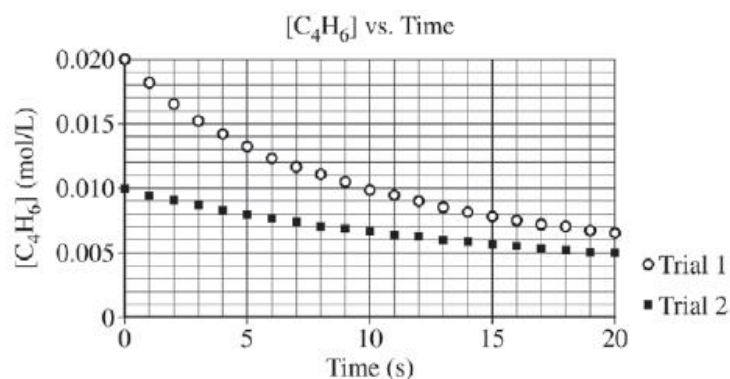
Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

- (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?





At high temperatures the compound  $\text{C}_4\text{H}_6$  (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.



- 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  $\text{C}_4\text{H}_6$ .
- Use the data plotted in the graphs to determine the order of the reaction with respect to  $\text{C}_4\text{H}_6$ .
- The initial rate of the reaction in trial 1 is  $0.0010 \text{ mol}/(\text{L} \cdot \text{s})$ . Calculate the rate constant,  $k$ , for the reaction at 625 K.

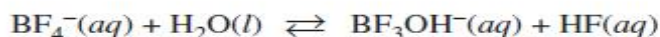




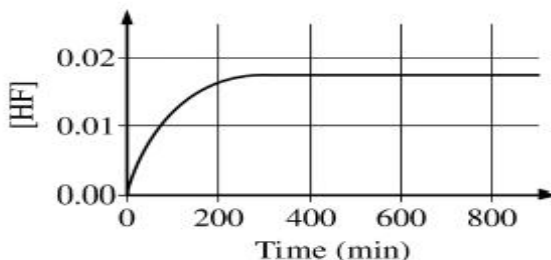
Tetrafluoroboric acid is a strong acid with the formula  $\text{HBF}_4$ . The acid can be prepared by reacting the weak acid  $\text{H}_3\text{BO}_3$  (molar mass 61.83 g/mol) with HF according to the equation above.

- (a) To prepare a solution of  $\text{BF}_4^-(aq)$ ,  $\text{HF}(g)$  is bubbled into a solution containing 50.0 g of  $\text{H}_3\text{BO}_3$  in a 1 L reaction vessel.
- Calculate the maximum number of moles of  $\text{BF}_4^-(aq)$  that can be produced.
  - Calculate the number of liters of  $\text{HF}(g)$ , measured at 273 K and 1.00 atm, that will be consumed if all the  $\text{H}_3\text{BO}_3$  reacts.
  - Will the pH of the solution increase, decrease, or remain the same during the course of the reaction? Justify your answer.

In another experiment, a 0.150 M  $\text{BF}_4^-(aq)$  solution is prepared by dissolving  $\text{NaBF}_4(s)$  in distilled water. The  $\text{BF}_4^-(aq)$  ions in the solution slowly react with  $\text{H}_2\text{O}(l)$  in the reversible reaction represented below.



The concentration of HF is monitored over time, as shown in the graph below.



[HF] reaches a constant value of 0.0174 M when the reaction reaches equilibrium. For the forward reaction, the rate law is  $\text{rate} = k_f [\text{BF}_4^-]$ . The value of the rate constant  $k_f$  was experimentally determined to be  $9.00 \times 10^{-4} \text{ min}^{-1}$ .

- (b) Calculate the rate of the forward reaction after 600. minutes. Include units with your answer.

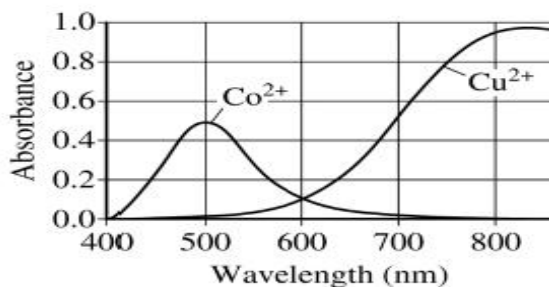
The rate law for the reverse reaction is  $\text{rate} = k_r [\text{BF}_3\text{OH}^-][\text{HF}]$ .

- (c) A student claims that the initial rate of the reverse reaction is equal to zero. Do you agree or disagree with this claim? Justify your answer in terms of the rate law for the reverse reaction.
- (d) At equilibrium the forward and reverse reaction rates are equal. Calculate the value of the rate constant for the reverse reaction.

A student has 100. mL of 0.400 M  $\text{CuSO}_4(aq)$  and is asked to make 100. mL of 0.150 M  $\text{CuSO}_4(aq)$  for a spectrophotometry experiment. The following laboratory equipment is available for preparing the solution: centigram balance, weighing paper, funnel, 10 mL beaker, 150 mL beaker, 50 mL graduated cylinder, 100 mL volumetric flask, 50 mL buret, and distilled water.

- (a) Calculate the volume of 0.400 M  $\text{CuSO}_4(aq)$  required for the preparation.
- (b) Briefly describe the essential steps to most accurately prepare the 0.150 M  $\text{CuSO}_4(aq)$  from the 0.400 M  $\text{CuSO}_4(aq)$  using the equipment listed above.

The student plans to conduct a spectrophotometric analysis to determine the concentration of  $\text{Cu}^{2+}(aq)$  in a solution. The solution has a small amount of  $\text{Co}(\text{NO}_3)_2(aq)$  present as a contaminant. The student is given the diagram below, which shows the absorbance curves for aqueous solutions of  $\text{Co}^{2+}(aq)$  and  $\text{Cu}^{2+}(aq)$ .



- (c) The spectrophotometer available to the student has a wavelength range of 400 nm to 700 nm. What wavelength should the student use to minimize the interference from the presence of the  $\text{Co}^{2+}(aq)$  ions?

Answer the following questions about ozone.

- (a) The  $\text{O}_3$  molecule has a central oxygen atom bonded to two outer oxygen atoms that are not bonded to one another. In the box below, draw the Lewis electron-dot diagram of the  $\text{O}_3$  molecule. Include all valid resonance structures.

- (b) Based on the diagram you drew in part (a), what is the shape of the ozone molecule?

Ozone decomposes according to the reaction represented below.

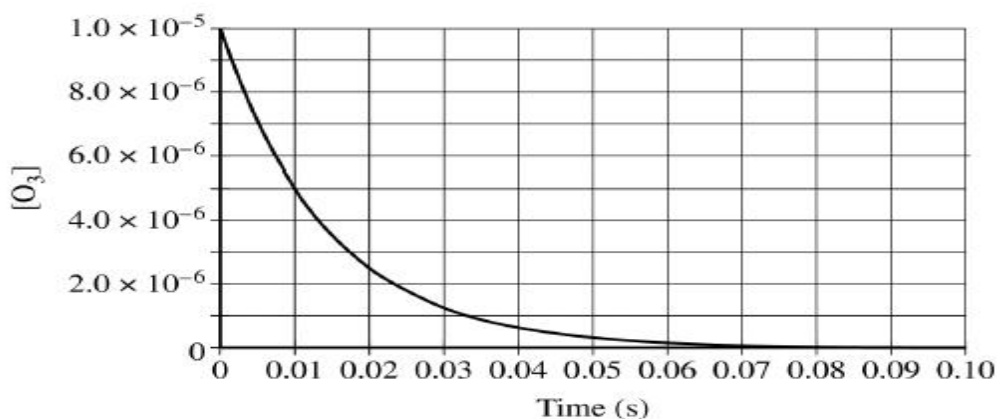


- (c) The bond enthalpy of the oxygen-oxygen bond in  $\text{O}_2$  is 498 kJ/mol. Based on the enthalpy of the reaction represented above, what is the average bond enthalpy, in kJ/mol, of an oxygen-oxygen bond in  $\text{O}_3$ ?

Ozone can oxidize  $\text{HSO}_3^-(aq)$ , as represented by the equation below.

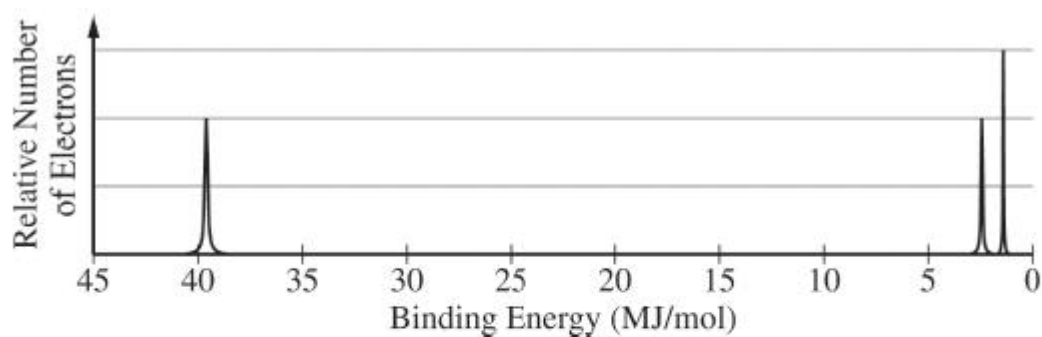


A solution is prepared in which the initial concentration of  $\text{HSO}_3^-(aq)$  ( $6.4 \times 10^{-4} M$ ) is much larger than that of  $\text{O}_3(aq)$  ( $1.0 \times 10^{-5} M$ ). The concentration of  $\text{O}_3(aq)$  is monitored as the reaction proceeds, and the data are plotted in the graph below.



- (d) The data are consistent with the following rate law:  $\text{rate} = k_1 [\text{O}_3]$ .

- Based on the graph on the previous page, determine the half-life of the reaction.
- Determine the value of the rate constant,  $k_1$ , for the rate law. Include units with your answer.
- Considering the relative concentrations of the reactants, briefly explain why the data in the graph are also consistent with the following rate law:  $\text{rate} = k_2 [\text{O}_3] [\text{HSO}_3^-]$ .
- Briefly describe an experiment that could provide evidence to support the rate law given in part (d)(iii).



The complete photoelectron spectrum of an element is represented above.

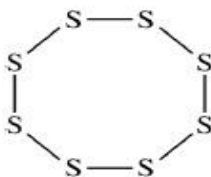
(a) Identify the element.

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.

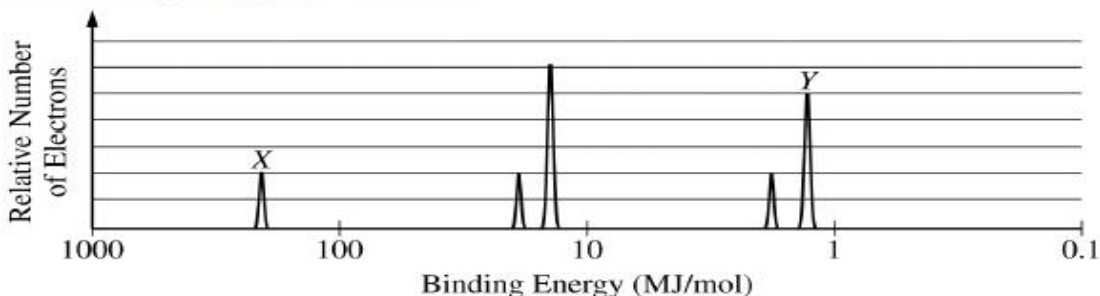
(c) If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.



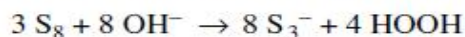


Elemental sulfur can exist as molecules with the formula  $S_8$ . The  $S_8$  molecule is represented by the incomplete Lewis diagram above.

- The diagram of  $S_8$  shows only bonding pairs of electrons. How many lone pairs of electrons does each S atom in the molecule have?
- Based on your answer to part (a), determine the expected value of the S–S–S bond angles in the  $S_8$  molecule.
- Write the electron configuration for the S atom in its ground state.
- The complete photoelectron spectrum for the element chlorine is represented below. Peak X in the spectrum corresponds to the binding energy of electrons in a certain orbital of chlorine atoms. The electrons in this orbital of chlorine have a binding energy of 273 MJ/mol, while the electrons in the same orbital of sulfur atoms have a binding energy of 239 MJ/mol.



- Identify the orbital and explain the difference between the binding energies in terms of Coulombic forces.
- Peak Y corresponds to the electrons in certain orbitals of chlorine atoms. On the spectrum shown, carefully draw the peak that would correspond to the electrons in the same orbitals of sulfur atoms.



In an experiment, a student studies the kinetics of the reaction represented above and obtains the data shown in the following table.

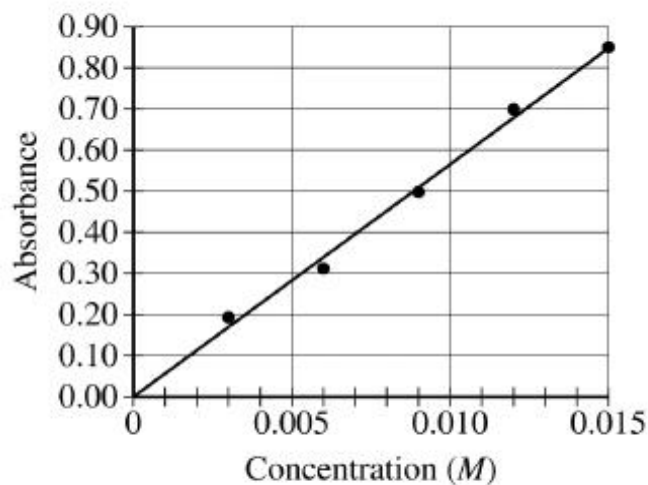
Experiment	Initial $[S_8]$ (M)	Initial $[OH^-]$ (M)	Initial Reaction Rate (M/s)
Trial 1	0.100	0.0100	0.699
Trial 2	0.300	0.0100	2.10
Trial 3	0.300	?	4.19

- Use the data in the table to do the following.
  - Determine the order of the reaction with respect to  $S_8$ . Justify your answer.
  - Determine the value of  $[OH^-]$  that was used in trial 3, considering that the reaction is first order with respect to  $OH^-$ . Justify your answer.

The next day the student conducts trial 4 using the same concentrations of  $S_8$  and  $OH^-$  as in trial 1, but the reaction occurs at a much slower rate than the reaction in trial 1. The student observes that the temperature in the lab is lower than it was the day before.

- Using particle-level reasoning, provide TWO explanations that help to account for the fact that the reaction rate is slower in trial 4.

To spectrophotometrically determine the mass percent of cobalt in an ore containing cobalt and some inert materials, solutions with known  $[\text{Co}^{2+}]$  are prepared and the absorbance of each of the solutions is measured at the wavelength of optimum absorbance. The data are used to create a calibration plot, shown below.



A 0.630 g sample of the ore is completely dissolved in concentrated  $\text{HNO}_3(aq)$ . The mixture is diluted with water to a final volume of 50.00 mL. Assume that all the cobalt in the ore sample is converted to  $\text{Co}^{2+}(aq)$ .

- What is the  $[\text{Co}^{2+}]$  in the solution if the absorbance of a sample of the solution is 0.74 ?
- Calculate the number of moles of  $\text{Co}^{2+}(aq)$  in the 50.00 mL solution.
- Calculate the mass percent of Co in the 0.630 g sample of the ore.