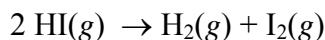


## Essay Questions

1983

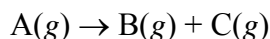
Graphical methods are frequently used to analyze data and obtain desired quantities.



The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

$T$ (K)	$k$ (liter/mol sec)
647	$8.58 \times 10^{-5}$
666	$2.19 \times 10^{-4}$
683	$5.11 \times 10^{-4}$
700	$1.17 \times 10^{-3}$
716	$2.50 \times 10^{-3}$

- (a) Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

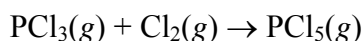


The following data give the partial pressure of A as a function of time and were obtained at 100°C for the reaction above.

$P_A$ (mm Hg)	$t$ (sec)
348	0
247	600
185	1200
105	2400
58	3600

- (b) Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.

1985

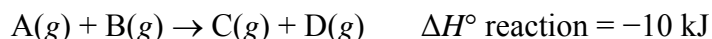


In the equation above, the forward reaction is first order in both  $\text{PCl}_3$  and  $\text{Cl}_2$  and the reverse reaction is first order in  $\text{PCl}_5$ .

- (a) Suppose that 2 moles of  $\text{PCl}_3$  and 1 mole of  $\text{Cl}_2$  are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of  $\text{PCl}_3$ ,  $\text{Cl}_2$ , and  $\text{PCl}_5$  change with time until after equilibrium has been firmly established.
- (b) Give the initial rate law for the forward reaction.
- (c) Provide a molecular explanation for the dependence of the rate of the forward reaction on the concentrations of the reactants.
- (d) Provide a molecular explanation for the dependence of the rate of the forward reaction on temperature.

1990

Consider the following general equation for a chemical reaction.

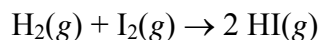


- Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.
- How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
- Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.



- Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

1992



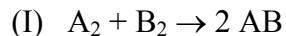
For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows.

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

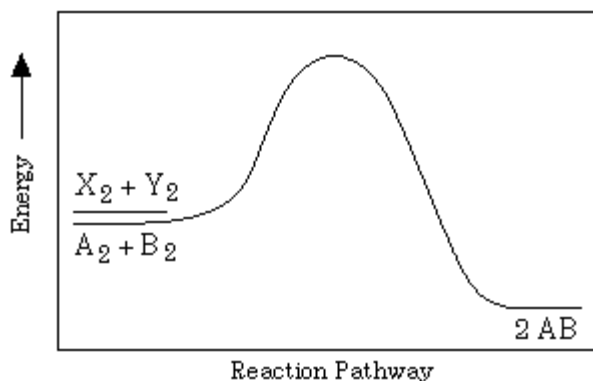
Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

- Addition of hydrogen gas at constant temperature and volume.
- Increase in volume of the reaction vessel at constant temperature.
- Addition of catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.
- Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

1995



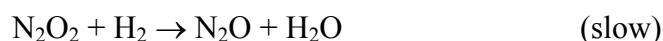
Two reactions are represented above. The potential energy diagram for reaction I is shown below. The potential energy of the reactants in reaction II is also indicated on the diagram. Reaction II is endothermic, and the activation energy of reaction I is greater than that of reaction II.



- (a) Complete the potential energy diagram for reaction II on the graph above.
- (b) For reaction I, predict how each of the following is affected as the temperature is increased by  $20^\circ\text{C}$ . Explain the basis for each prediction.
- Rate of reaction
  - Heat of reaction
- (c) For reaction II, the form of the rate law is  $rate = k[X_2]^m[Y_2]^n$ . Briefly describe an experiment that can be conducted in order to determine the values of  $m$  and  $n$  in the rate law for the reaction.
- (d) From the information given, determine which reaction initially proceeds at the faster rate under the same conditions of concentration and temperature. Justify your answer.

1996

The reaction between NO and  $H_2$  is believed to occur in the following three-step process.



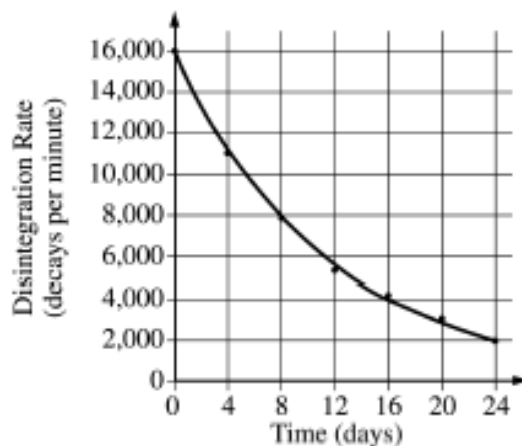
- (a) Write a balanced equation for the overall reaction.
- (b) Identify the intermediates in the reaction. Explain your reasoning.
- (c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is  $rate = k[NO]^2[H_2]$ . The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an  $H_2$  molecule. Are conclusions (1) and (2) correct? Explain.
- (d) Explain why an increase in temperature increases the rate constant,  $k$ , given the rate law in (c).

2003

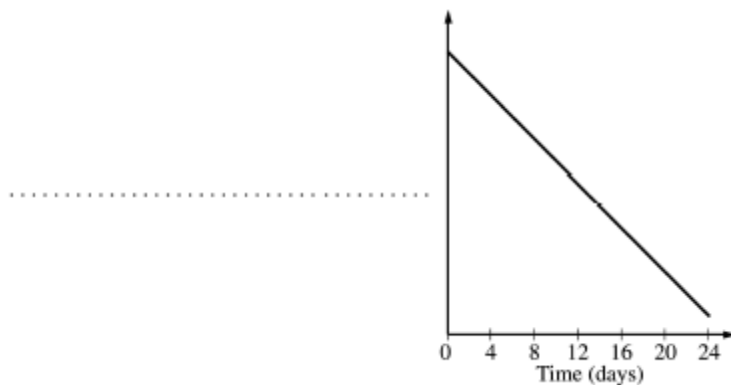
The decay of the radioisotope I-131 was studied in a laboratory. I-131 is known to decay by beta ( ${}_{-1}^0e$ ) emission.

- (a) Write a balanced nuclear equation for the decay of I-131.
- (b) What is the source of the beta particle emitted from the nucleus?

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



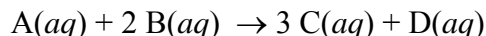
- (c) Determine the half-life,  $t_{1/2}$ , of I-131 using the graph above.
- (d) The data can be used to show that the decay of I-131 is a first-order reaction, as indicated on the graph below.



- (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.

## Problems

1981



For the reaction above, carried out in solution of 30°C, the following kinetic data were obtained:

Experiment	Initial Conc. of Reactants (mole liter <sup>-1</sup> )		Initial Rate of Reaction (mole liter <sup>-1</sup> ·hr <sup>-1</sup> )
	A <sub>0</sub>	B <sub>0</sub>	
1	0.240	0.480	8.00
2	0.240	0.120	2.00
3	0.360	0.240	9.00
4	0.120	0.120	0.500
5	0.240	0.0600	1.00
6	0.0140	1.35	?

- Write the rate-law expression for this reaction.
- Calculate the value of the specific rate constant  $k$  at 30°C and specify its units.
- Calculate the value of the initial rate of this reaction at 30°C for the initial concentrations shown in experiment 6.
- Assume that the reaction goes to completion. Under the conditions specified for experiment 2, what would be the final molar concentration of C?

1984

For a hypothetical chemical reaction that has the stoichiometry  $2 X + Y \rightarrow Z$ , the following initial rate data were obtained. All measurements were made at the same temperature.

Initial Rate of Formation of Z, (mol L <sup>-1</sup> sec <sup>-1</sup> )	Initial [X] <sub>0</sub> , (mol L <sup>-1</sup> )	Initial [Y] <sub>0</sub> , (mol L <sup>-1</sup> )
$7.0 \times 10^{-4}$	0.20	0.10
$1.4 \times 10^{-3}$	0.40	0.20
$2.8 \times 10^{-3}$	0.40	0.40
$4.2 \times 10^{-3}$	0.60	0.60

- Give the rate law for this reaction from the data above.
- Calculate the specific rate constant for this reaction and specify its units.
- How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are  $[X]_0 = 0.80$  molar,  $[Y]_0 = 0.60$  molar and  $[Z]_0 = 0$  molar?
- Select from the mechanisms below the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates.
  - $X + Y \rightarrow M$  (slow)  
 $X + M \rightarrow Z$  (fast)
  - $X + X \rightleftharpoons M$  (fast)  
 $Y + M \rightarrow Z$  (slow)
  - $Y \rightarrow M$  (slow)  
 $M + X \rightarrow N$  (fast)  
 $N + X \rightarrow Z$  (fast)

1987

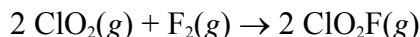


The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table

Experiment	Initial [HgCl <sub>2</sub> ]	Initial [C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> ]	Initial Rate of Formation of Cl <sup>-</sup> (mol L <sup>-1</sup> min <sup>-1</sup> )
1	0.0836	0.202	0.52 × 10 <sup>-4</sup>
2	0.0836	0.404	2.08 × 10 <sup>-4</sup>
3	0.0418	0.404	1.06 × 10 <sup>-4</sup>
4	0.0316	?	1.27 × 10 <sup>-4</sup>

- (a) According to the data shown, what is the rate law for the reaction above?  
 (b) On the basis of the rate law determined in part (a), calculate the specific rate constant. Specify the units.  
 (c) What is the numerical value for the initial rate of disappearance of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> for Experiment 1?  
 (d) Calculate the initial oxalate ion concentration for Experiment 4.

1991



The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial [ClO <sub>2</sub> ], (mol L <sup>-1</sup> )	Initial [F <sub>2</sub> ], (mol L <sup>-1</sup> )	Initial Rate of Increase of [ClO <sub>2</sub> F], (mol L <sup>-1</sup> sec <sup>-1</sup> )
1	0.010	0.10	2.4 × 10 <sup>-3</sup>
2	0.010	0.40	9.6 × 10 <sup>-3</sup>
3	0.020	0.20	9.6 × 10 <sup>-3</sup>

- (a) Write the rate law expression for the reaction above.  
 (b) Calculate the numerical value of the rate constant and specify the units.  
 (c) In experiment 2, what is the initial rate of decrease of [F<sub>2</sub>]?  
 (d) Which of the following reaction mechanisms is consistent with the rate law developed in (a). Justify your choice.

- I.  $\text{ClO}_2 + \text{F}_2 \rightleftharpoons \text{ClO}_2\text{F}_2$  (fast)  
 $\text{ClO}_2\text{F}_2 \rightarrow \text{ClO}_2\text{F} + \text{F}$  (slow)  
 $\text{ClO}_2 + \text{F} \rightarrow \text{ClO}_2\text{F}$  (fast)
- II.  $\text{F}_2 \rightarrow 2 \text{F}$  (slow)  
 $2 (\text{ClO}_2 + \text{F} \rightarrow \text{ClO}_2\text{F})$  (fast)

2003



In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial $[\text{Br}^-]$ (mol L <sup>-1</sup> )	Initial $[\text{BrO}_3^-]$ (mol L <sup>-1</sup> )	Initial $[\text{H}^+]$ (mol L <sup>-1</sup> )	Rate of Disappearance of $\text{BrO}_3^-$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.00100	0.00500	0.100	$2.50 \times 10^{-4}$
2	0.00200	0.00500	0.100	$5.00 \times 10^{-4}$
3	0.00100	0.00750	0.100	$3.75 \times 10^{-4}$
4	0.00100	0.01500	0.200	$3.00 \times 10^{-3}$

- (a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.
- $\text{Br}^-$
  - $\text{BrO}_3^-$
  - $\text{H}^+$
- (b) Write the rate law for the overall reaction.
- (c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.
- (d) Calculate the value of the standard cell potential,  $E^\circ$ , for the reaction using the information in the table below.

Half-reaction	$E^\circ$ (V)
$\text{Br}_2(l) + 2 e^- \rightarrow 2 \text{Br}^-(aq)$	+1.065
$\text{BrO}_3^-(aq) + 6 \text{H}^+(aq) + 5 e^- \rightarrow \frac{1}{2} \text{Br}_2(l) + 3 \text{H}_2\text{O}(l)$	+1.52

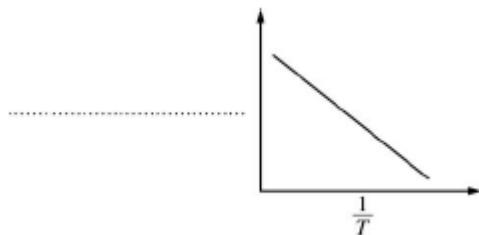
- (e) Determine the total number of electrons transferred in the overall reaction.

2004

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	?

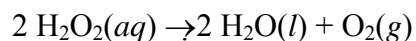
- (a) Calculate the initial concentration of the colored species.
- (b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
- (c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
- (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) Label the vertical axis of the graph.
- (ii) Explain how to calculate the activation energy from this graph.



2004B

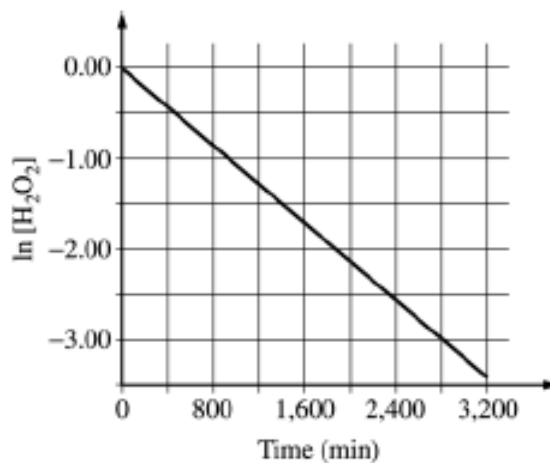
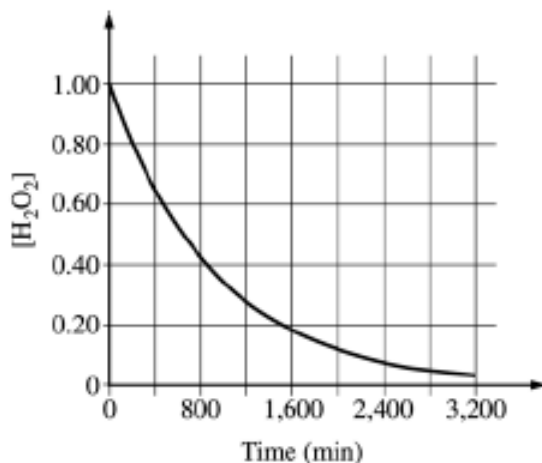


Hydrogen peroxide decomposes according to the equation above.

(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.

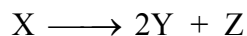
- The original number of moles of  $\text{H}_2\text{O}_2$  in a 125 mL sample of the 6.00 percent  $\text{H}_2\text{O}_2$  solution
- The number of moles of  $\text{O}_2(g)$  that are produced when all of the  $\text{H}_2\text{O}_2$  in the 125 mL sample decomposes

(b) The graphs below show results from a study of the decomposition of  $\text{H}_2\text{O}_2$ .



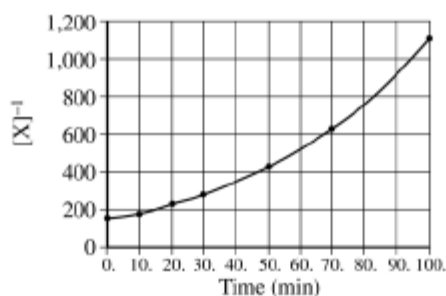
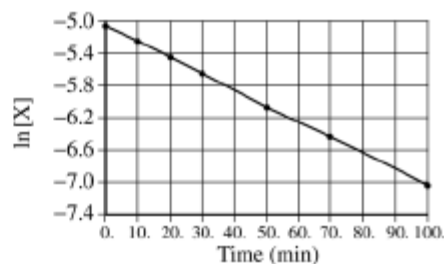
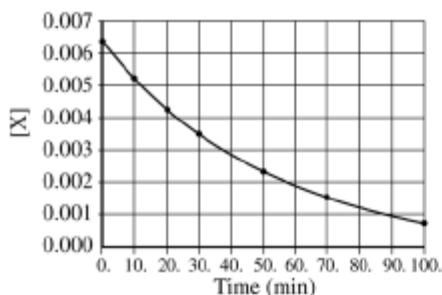
- Write the rate law for the reaction. Justify your answer.
- Determine the half-life of the reaction.
- Calculate the value of the rate constant,  $k$ . Include appropriate units in your answer.
- Determine  $[\text{H}_2\text{O}_2]$  after 2,000 minutes elapse from the time the reaction began.

2005B



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.