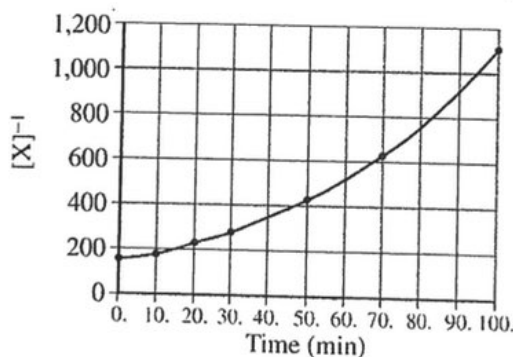
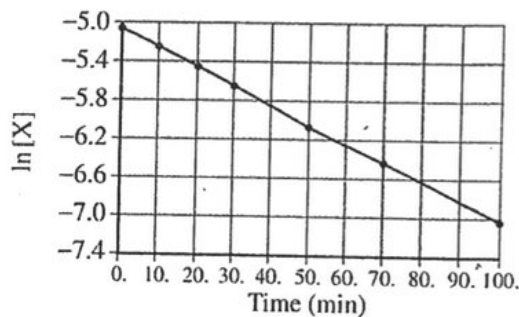
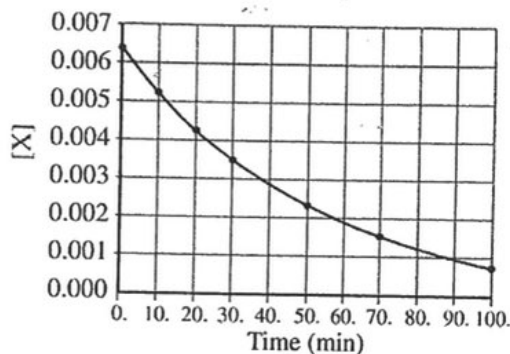




1

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 ⁻¹)	ln [X]	[X] ⁻¹ (L mol ⁻¹)
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



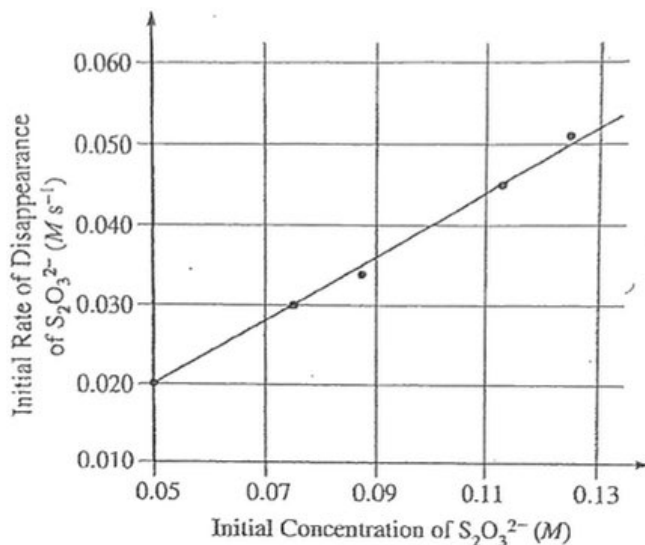
- How many moles of X were initially in the flask?
- How many molecules of Y were produced in the first 20. minutes of the reaction?
- What is the order of this reaction with respect to X? Justify your answer.
- Write the rate law for this reaction.
- Calculate the specific rate constant for this reaction.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

2



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 $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (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 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 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.

3



Consider the reaction represented above.

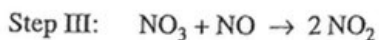
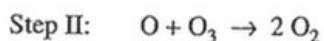
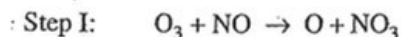
- (a) Referring to the data in the table below, calculate the standard enthalpy change, ΔH° , for the reaction at 25°C. Be sure to show your work.

	$\text{O}_3(\text{g})$	$\text{NO}(\text{g})$	$\text{NO}_2(\text{g})$
Standard enthalpy of formation, ΔH_f° , at 25°C (kJ mol ⁻¹)	143	90.	33

- (b) Make a qualitative prediction about the magnitude of the standard entropy change, ΔS° , for the reaction at 25°C. Justify your answer.
- (c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, ΔG° , for the reaction at 25°C. Explain your reasoning.
- (d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[\text{O}_3]$ (mol L ⁻¹)	Initial $[\text{NO}]$ (mol L ⁻¹)	Initial Rate of Formation of NO_2 (mol L ⁻¹ s ⁻¹)
1	0.0010	0.0010	x
2	0.0010	0.0020	$2x$
3	0.0020	0.0010	$2x$
4	0.0020	0.0020	$4x$

- (e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

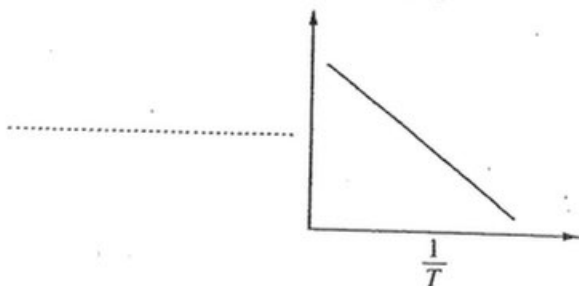


4

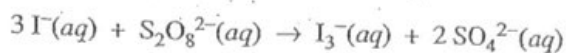
The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of $5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ and the path length of the cuvette 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
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-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.

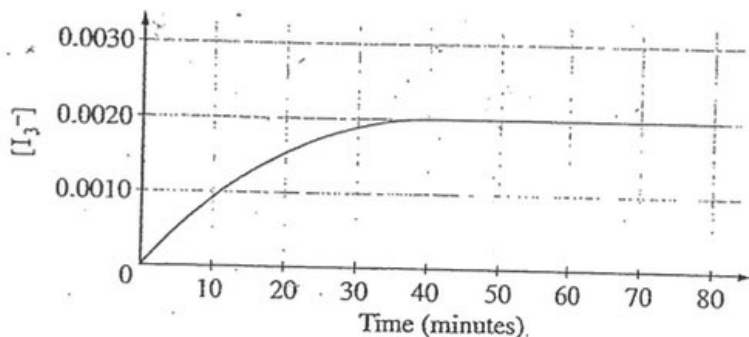


5

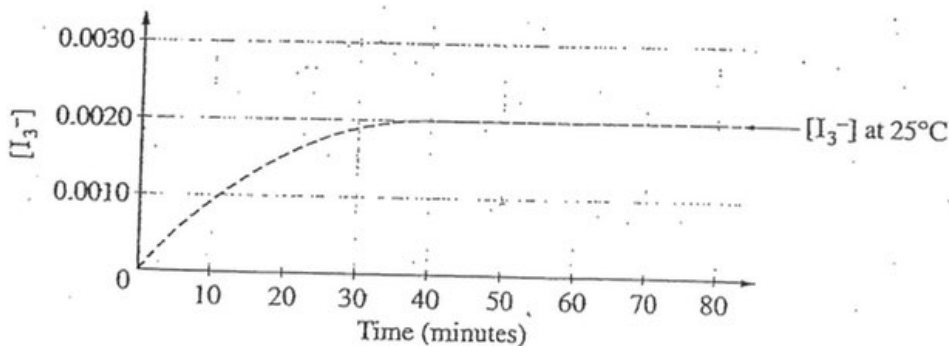


Iodide ion, $\text{I}^-(aq)$, reacts with peroxydisulfate ion, $\text{S}_2\text{O}_8^{2-}(aq)$, according to the equation above. Assume that the reaction goes to completion.

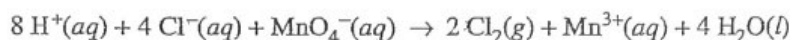
- (a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert $\text{I}^-(aq)$ to $\text{I}_3^-(aq)$.
- (b) In an experiment, equal volumes of $0.0120 \text{ M I}^-(aq)$ and $0.0040 \text{ M S}_2\text{O}_8^{2-}(aq)$ are mixed at 25°C . The concentration of $\text{I}_3^-(aq)$ over the following 80 minutes is shown in the graph below.



- (i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning.
- (ii) Explain how to determine the instantaneous rate of formation of $\text{I}_3^-(aq)$ at exactly 20 minutes. Draw on the graph above as part of your explanation.
- (c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to $\text{I}^-(aq)$ and with respect to $\text{S}_2\text{O}_8^{2-}(aq)$.
- (d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant, k , for the reaction.
- (e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at 35°C rather than at 25°C .



6



$\text{Cl}_2(g)$ 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 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.
- Cl^-
 - 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:
- 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.