



Kinetics Cheat Sheet

Relationships

Differential Rate Law (concentration vs. rate data): $\text{Rate} = k [A]^x [B]^y$

Integrated Rate Laws (concentration vs. time data):

Zero order	$[A] = (-)kt + [A]_0$
First order	$\ln [A] = (-)kt + \ln[A]_0$
Second order	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$t_{1/2} = \frac{0.693}{k}$ for first order reactions and all nuclear decay

Connections

Stoichiometry – “using up” one component of the system might indicate a limiting reactant in effect

Electrochemistry – if reaction is redox in nature, rate problems could come into play

Thermochemistry – E_a and $\Delta H^\circ_{\text{rxn}}$ and reaction diagrams

Potential Pitfalls

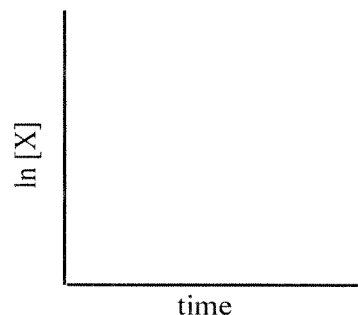
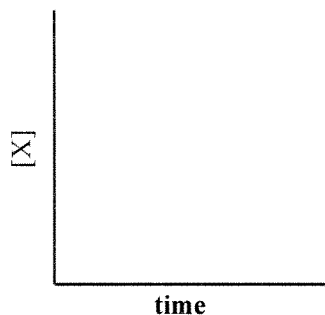
Units on k ! Make sure you can solve for units for k



NMSI SUPER PROBLEM

The decomposition of substance X was experimentally observed at 25°C and shown to be first order with respect to X. Data from the experiment are shown below.

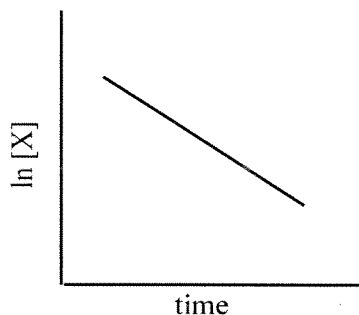
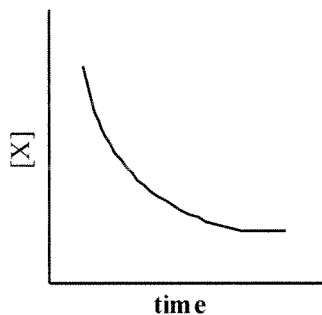
[X] M	Time (min)
0.100	0
0.088	2
0.069	6
0.054	10
0.043	14
0.030	???



(a) For each of the graphs above

i. Sketch the expected curve based on the labeled axes. You do not need to plot the exact data.

Since the reaction is first order, the plot of $\ln [X]$ v. t is linear while the plot of $[X]$ vs. t should show the non-linear decrease in $[X]$.



1 point is earned for sketching the plot of $\ln [X]$ as linear with a negative slope.

1 point is earned for sketching the plot of $[X]$ as non-linear, decreasing over time.

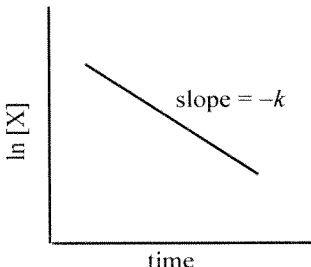
ii. Write the rate law for the decomposition of substance X.

Since the reaction is decomposition and first order overall the rate law is $\text{rate} = k [X]$

1 point is earned for the correct rate law.



- iii. Explain how one of the two graphs above can be used to determine the rate constant, k . Be sure to specify which graph.

<p>The slope of the plot of $\ln [X]$ v. t is equal to the absolute value of the rate constant, k.</p> 	<p>1 point is earned for identify the slope of the plot of $\ln[X]$ vs. t will be equal to the rate constant, k.</p>
---	--

(b) Based on the above data

- i. Calculate the rate constant for this reaction. Be sure to include units.

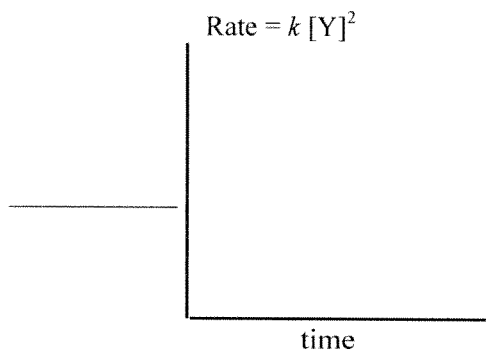
$\ln \frac{[A]}{[A]_0} = -kt$ $\ln \frac{[0.043]}{[0.100]} = -(k)14$ $0.0603 \text{ min}^{-1} = k$	<p>1 point is earned for the value and the sign of the rate constant.</p> <p>1 point is earned for the correct units (any time^{-1} earns the point)</p> <p>The points can be earned with a description of how the slope of the line was determined with a graphing calculator.</p>
--	---

- ii. How many minutes will it take for $[X]$ to become $0.030 M$?

$\ln \frac{[A]}{[A]_0} = -kt$ $\ln \frac{[0.030]}{[0.100]} = -(0.0603)t$ $20 \text{ min} = t$	<p>1 point is earned for the substitution.</p> <p>1 point is earned for the correct answer.</p> <p>These points can be earned with a description of how the data was extrapolated using a graphing calculator.</p>
---	--

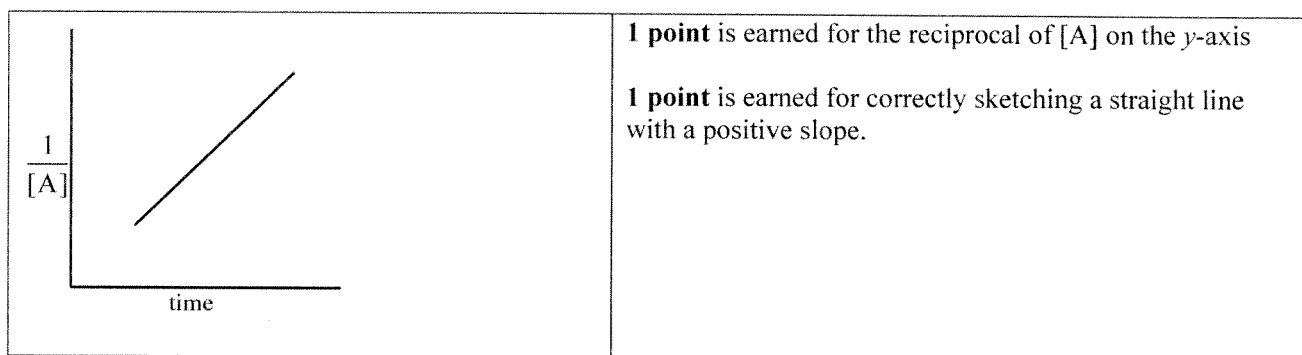


In a different experiment, the decomposition of substance Y at 50°C was determined to have the following rate law.



(c) On the axes above

- i. Sketch the graph that is expected to provide a linear relationship when plotted against time. Be sure to label the y-axis.



- ii. What does the slope of this line represent?

Slope = k	1 point is earned for stating that slope = k
-------------	---

(d) The temperature of this reaction was increased from 50°C to 100°C. Predict the effect this would have on each of the following.

- i. Rate of the reaction

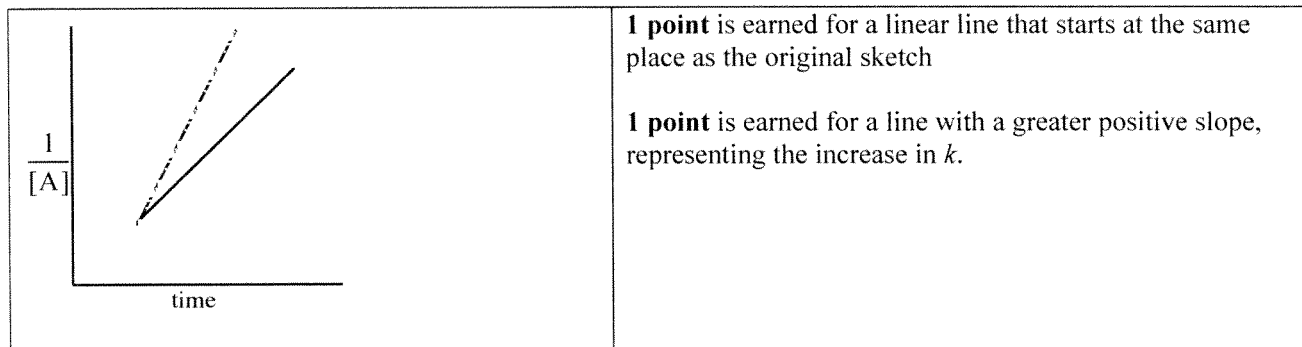
The 50°C increase in temperature will increase the rate of the reaction	1 point is earned for stating that the rate increases
---	--

- ii. Rate constant, k

The rate constant, k will increase	1 point is earned for stating that rate constant, k increases
--------------------------------------	--

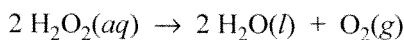


(e) Sketch the graph of the reaction at 100°C on the plot in part (c)



AP[®] CHEMISTRY
2004 SCORING GUIDELINES (Form B)

Question 3



3. Hydrogen peroxide decomposes according to the equation above.

(a) An aqueous solution of H_2O_2 that is 6.00 percent H_2O_2 by mass has a density of 1.03 g mL^{-1} . Calculate each of the following.

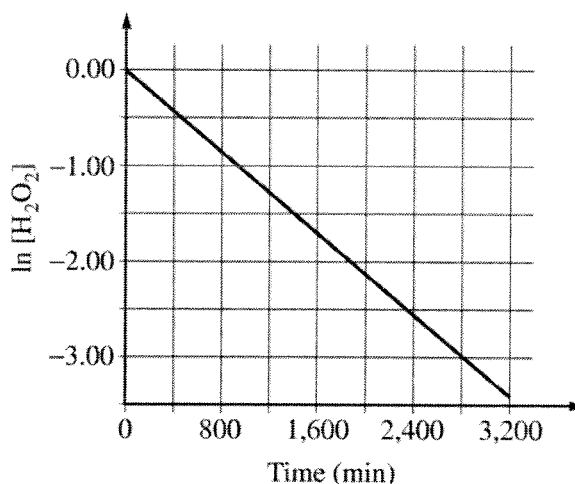
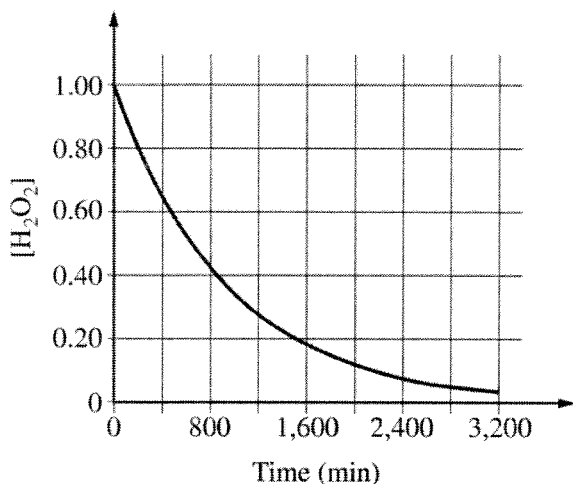
(i) The original number of moles of H_2O_2 in a 125 mL sample of the 6.00 percent H_2O_2 solution

$n_{\text{H}_2\text{O}_2} = 125 \text{ mL H}_2\text{O}_2(aq) \times \frac{1.03 \text{ g H}_2\text{O}_2(aq)}{1.00 \text{ mL H}_2\text{O}_2(aq)} \times \frac{6.00 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}_2(aq)} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0 \text{ g H}_2\text{O}_2} = 0.227 \text{ mol H}_2\text{O}_2$	1 point for determining mass of $\text{H}_2\text{O}_2(aq)$ 1 point for mass of H_2O_2 1 point for moles of H_2O_2
---	---

(ii) The number of moles of $\text{O}_2(g)$ that are produced when all of the H_2O_2 in the 125 mL sample decomposes

$n_{\text{O}_2} = 0.227 \text{ mol H}_2\text{O}_2 \times \frac{1 \text{ mol O}_2(g)}{2 \text{ mol H}_2\text{O}_2(aq)} = 0.114 \text{ mol O}_2(g)$	1 point for moles of $\text{O}_2(g)$
---	--------------------------------------

(b) The graphs below show results from a study of the decomposition of H_2O_2 .



AP[®] CHEMISTRY
2004 SCORING GUIDELINES (Form B)

Question 3 (cont'd.)

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

rate = $k[\text{H}_2\text{O}_2]^1$	1 point for correct rate law
A plot of $\ln[\text{H}_2\text{O}_2]$ versus time is a straight line, so the reaction follows simple first-order kinetics.	1 point for explanation

- (ii) Determine the half-life of the reaction.

Using the graph showing $[\text{H}_2\text{O}_2]$ versus time, the half-life is about 650 minutes.	
<i>OR</i>	
Calculate from $t_{1/2} = \frac{0.693}{k}$ after determining k from the slope in part (b)(iii)	1 point for a half-life between 600 and 700 minutes

- (iii) Calculate the value of the rate constant, k . Include appropriate units in your answer.

$t_{1/2} = \frac{0.693}{k}$	
$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{650 \text{ min}} = 1.1 \times 10^{-3} \text{ min}^{-1}$	1 point for the magnitude of the rate constant
<i>OR</i>	1 point for the units
k can be obtained from the determination of the slope of the line in the $\ln k$ versus time plot	

- (iv) Determine $[\text{H}_2\text{O}_2]$ after 2,000 minutes elapse from the time the reaction began.

From the graph of $[\text{H}_2\text{O}_2]$ versus time, $[\text{H}_2\text{O}_2]$ is approximately 0.12 M .	
<i>OR</i>	
From the graph of $\ln[\text{H}_2\text{O}_2]$ versus time, $\ln[\text{H}_2\text{O}_2]$ is approximately -2.2 , so $[\text{H}_2\text{O}_2] = e^{-2.2} = 0.11 M$	1 point for $0.09 < [\text{H}_2\text{O}_2] < 0.13 M$

AP[®] CHEMISTRY
2012 SCORING GUIDELINES

Question 3
(9 points)



A sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, S° , in $\text{J}/(\text{mol}\cdot\text{K})$ at 298 K
$\text{CH}_3\text{CH}_2\text{NH}_2(\text{g})$	284.9
$\text{CH}_2\text{CH}_2(\text{g})$	219.3
$\text{NH}_3(\text{g})$	192.8

- (a) Using the data in the table above, calculate the value, in $\text{J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$, of the standard entropy change, ΔS° , for the reaction at 298 K.

$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$ $\Delta S^\circ_{\text{rxn}} = [(219.3 + 192.8) - 284.9] \text{ J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$ $= 127.2 \text{ J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$	1 point is earned for the correct ΔS° .
--	--

- (b) Using the data in the table below, calculate the value, in $\text{kJ}/\text{mol}_{\text{rxn}}$, of the standard enthalpy change, ΔH° , for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

$\Delta H^\circ = \text{enthalpy of bonds broken} - \text{enthalpy of bonds formed}$ $\Delta H^\circ = [5(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}}) + 2(\Delta H_{\text{N-H}})] -$ $[4(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C=C}}) + 3(\Delta H_{\text{N-H}})]$ $= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49 \text{ kJ}/\text{mol}_{\text{rxn}}$ <p style="text-align: center;">OR</p> $\Delta H^\circ = [(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}})] - [(\Delta H_{\text{C=C}}) + (\Delta H_{\text{N-H}})]$ $= [413 + 293 + 348] \text{ kJ}/\text{mol} - [614 + 391] \text{ kJ}/\text{mol} = 49 \text{ kJ}/\text{mol}_{\text{rxn}}$	<p>1 point is earned for the correct bond count and use of values from table.</p> <p>1 point is earned for the correct setup in terms of bonds broken minus bonds formed and calculated ΔH°.</p>
---	--

AP[®] CHEMISTRY
2012 SCORING GUIDELINES

Question 3 (continued)

- (c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive ΔH° .

1 point is earned for the correct choice with explanation.

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $\text{CH}_3\text{CH}_2\text{NH}_2$ is found to be 3.60×10^{-4} mol/L.

- (d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

$$\ln[A]_t - \ln[A]_o = -kt$$

$$\ln(3.60 \times 10^{-4} \text{ mol/L}) - \ln\left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right) = -k(20.0 \text{ min})$$

$$-7.929 - (-6.053) = -k(20.0 \text{ min})$$

$$k = 9.38 \times 10^{-2} \text{ min}^{-1}$$

1 point is earned for the initial concentration of $\text{CH}_3\text{CH}_2\text{NH}_2$.

1 point is earned for the correct setup of the first order integrated rate law equation.

1 point is earned for the calculated result with unit.

- (e) Calculate the initial rate, in $M \text{ min}^{-1}$, of the reaction at 773 K.

$$\begin{aligned} \text{initial rate} &= k[\text{CH}_3\text{CH}_2\text{NH}_2] = (9.38 \times 10^{-2} \text{ min}^{-1})\left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right) \\ &= 2.20 \times 10^{-4} M \text{ min}^{-1} \end{aligned}$$

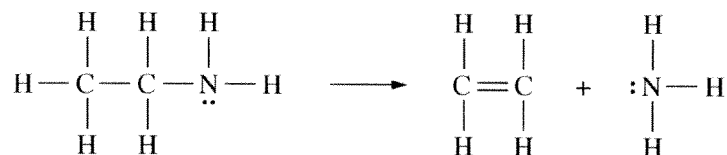
1 point is earned for the calculated result.

- (f) If $\frac{1}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

The plot would produce a curve; had the reaction been second order the plot would have been a straight line. A plot of $\ln[\text{CH}_3\text{CH}_2\text{NH}_2]$ vs. t would have yielded a straight line.

1 point is earned for the correct choice with explanation.

2012 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS



3. A sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, S° , in $\text{J}/(\text{mol}\cdot\text{K})$ at 298 K
$\text{CH}_3\text{CH}_2\text{NH}_2(g)$	284.9
$\text{CH}_2\text{CH}_2(g)$	219.3
$\text{NH}_3(g)$	192.8

- (a) Using the data in the table above, calculate the value, in $\text{J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$, of the standard entropy change, ΔS° , for the reaction at 298 K.
- (b) Using the data in the table below, calculate the value, in $\text{kJ}/\text{mol}_{\text{rxn}}$, of the standard enthalpy change, ΔH° , for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

- (c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $\text{CH}_3\text{CH}_2\text{NH}_2$ is found to be 3.60×10^{-4} mol/L.

- (d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.
- (e) Calculate the initial rate, in $M \text{ min}^{-1}$, of the reaction at 773 K.
- (f) If $\frac{1}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

STOP

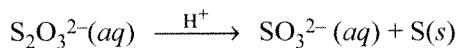
**If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.**

© 2012 The College Board.
Visit the College Board on the Web: www.collegeboard.org.

GO ON TO THE NEXT PAGE.

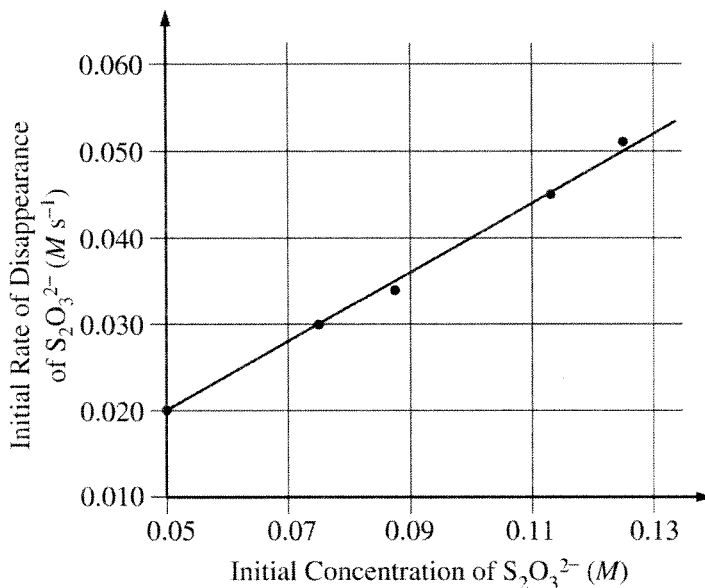
AP[®] CHEMISTRY
2009 SCORING GUIDELINES (Form B)

Question 2 (8 points)



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



- (a) Identify the independent variable in the experiment.

The initial concentration of $\text{S}_2\text{O}_3^{2-}(\text{aq})$	One point is earned for the correct answer.
---	---

- (b) Determine the order of the reaction with respect to $\text{S}_2\text{O}_3^{2-}$. Justify your answer by using the information above.

<p>Using trials 1 and 2:</p> $\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[\text{S}_2\text{O}_3^{2-}]^{m_2}}{k_1[\text{S}_2\text{O}_3^{2-}]^{m_1}}$ $\frac{0.030 \text{ M s}^{-1}}{0.020 \text{ M s}^{-1}} = \frac{[0.075]^m}{[0.050]^m}$ <p>$1.5 = (1.5)^m$, so $m = 1$ and the reaction is first order with respect to $\text{S}_2\text{O}_3^{2-}$.</p> <p><u>Note:</u> Other correct justifications are acceptable.</p>	<p>One point is earned for the correct order.</p> <p>One point is earned for a correct justification.</p>
---	---

AP[®] CHEMISTRY
2009 SCORING GUIDELINES (Form B)

Question 2 (continued)

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

$\text{rate} = k [\text{S}_2\text{O}_3^{2-}] \Rightarrow k = \frac{\text{rate}}{[\text{S}_2\text{O}_3^{2-}]}$ <p>Using the data from trial 1, $k = \frac{0.020 \text{ M s}^{-1}}{0.050 \text{ M}} = \mathbf{0.40 \text{ s}^{-1}}$</p> <p>OR</p> <p>the rate constant is equal to the slope of the line</p> $k = \frac{(0.052 - 0.020) \text{ M s}^{-1}}{(0.13 - 0.05) \text{ M}} = \frac{0.032 \text{ M s}^{-1}}{0.08 \text{ M}} = \mathbf{0.40 \text{ s}^{-1}}$	<p>One point is earned for the correct value.</p> <p>One point is earned for the correct units.</p>
--	---

- (d) In another trial the student mixed $0.10 \text{ M Na}_2\text{S}_2\text{O}_3$ 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 .

$\ln[A]_t - \ln[A]_0 = -kt \Rightarrow \ln \frac{[A]_t}{[A]_0} = -kt$ $\ln \frac{[\text{S}_2\text{O}_3^{2-}]_t}{[\text{S}_2\text{O}_3^{2-}]_0} = -kt$ $\ln \frac{0.020}{0.10} = (-0.40 \text{ s}^{-1})(t) \Rightarrow t = \frac{-1.61}{-0.40 \text{ s}^{-1}} = \mathbf{4.0 \text{ s}}$	<p>One point is earned for the correct setup.</p> <p>One point is earned for the correct answer with units.</p>
--	---

- (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.

<p>The line drawn should start on the y-axis at a lower point than the line already plotted and should have a less steep slope.</p>	<p>One point is earned for an acceptable line.</p>
---	--

AP[®] CHEMISTRY
2004 SCORING GUIDELINES

Question 3

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.

$A = abc$ $c = \frac{A}{ab} = \frac{0.600}{(5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})}$ $= 1.20 \times 10^{-4} \text{ M}$ <p style="text-align: center;"><u>OR</u></p> $A_0 = abc_0 \quad A_1 = abc_1$ $\frac{A_0}{c_0} = \frac{A_1}{c_1} \quad \frac{0.600}{c_0} = \frac{0.200}{4.00 \times 10^{-5}}$ $c_0 = 1.20 \times 10^{-4} \text{ M}$	<p style="text-align: center;">1 point for concentration of X</p>
--	---

(b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.

<p>Using the first two readings,</p> $\ln[X]_t - \ln[X]_0 = -kt \quad \text{OR} \quad \ln \frac{[X]_t}{[X]_0} = -kt$ $\ln \frac{4.00 \times 10^{-5}}{1.20 \times 10^{-4}} = -k(35.0 \text{ min})$ $\ln(0.333) = -k(35.0 \text{ min})$ $-1.10 = -k(35.0 \text{ min})$ $k = 3.14 \times 10^{-2} \text{ min}^{-1}$	<p style="text-align: center;">1 point for magnitude and correct sign of rate constant</p> <p style="text-align: center;">1 point for correct units</p>
---	---

AP[®] CHEMISTRY
2004 SCORING GUIDELINES

Question 3 (cont'd.)

(c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.

$\ln \frac{[X]_t}{[X]_0} = -k t$ $\ln \frac{1.50 \times 10^{-5}}{1.20 \times 10^{-4}} = (-3.14 \times 10^{-2} \text{ min}^{-1}) t$ $\ln (0.125) = (-3.14 \times 10^{-2} \text{ min}^{-1}) t$ $-2.08 = (-3.14 \times 10^{-2} \text{ min}^{-1}) t$ $t = 66.2 \text{ min}$	<p>1 point for correct substitution</p> <p>1 point for correct answer</p> <p><u>Note:</u> students may use half-lives to answer this question.</p>
---	--

(d) Calculate the half-life of the reaction. Include units with your answer.

$\ln \frac{[X]_t}{[X]_0} = -k t$ $\ln \frac{0.5 [X]_0}{[X]_0} = (-3.14 \times 10^{-2} \text{ min}^{-1}) t_{1/2}$ $\ln (0.5) = (-3.14 \times 10^{-2} \text{ min}^{-1}) t_{1/2}$ $-0.693 = (-3.14 \times 10^{-2} \text{ min}^{-1}) t_{1/2}$ $22.1 \text{ min} = t_{1/2}$ <p style="text-align: center;"><u>OR</u></p> $t_{1/2} = \frac{0.693}{k}$ $t_{1/2} = \frac{0.693}{3.14 \times 10^{-2} \text{ min}^{-1}} = 22.1 \text{ min}$	<p>1 point for correct magnitude</p> <p>1 point for the correct units</p> <p>(1 point for the half-life equation if no k is given)</p>
---	---

(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.

The vertical axis should be labeled $\ln k$.	1 point
---	---------

AP[®] CHEMISTRY
2004 SCORING GUIDELINES

Question 3 (cont'd.)

- (ii) Explain how to calculate the activation energy from this graph.

<p>The slope of the line is related to the activation energy:</p> $\text{slope} = -\frac{E_a}{R}$ <p>To determine the activation energy for the reaction, multiply the slope by $-8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.</p>	<p>1 point for recognizing that the slope must be measured</p> <p>1 point for the correct explanation of how to obtain the activation energy</p>
--	--

