AP® Chemistry (Operational)
2004 Sample Student Responses

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 $5.00 \times 10^3\ cm^{-1}\ M^{-1}$ 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.

$A = a \cdot b \cdot c$

[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	?

rate = k[x] mol/L mol L⁻¹ min⁻¹

(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.

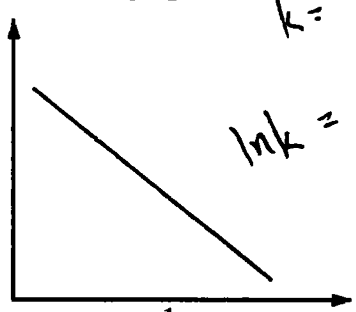
$k = A e^{-\frac{E_a}{RT}}$

$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$

$\ln k \propto \frac{1}{T}$

$-\frac{E_a}{R} = m$

ln k



a) Absorbance = a · b · [x]

∴ [x] = (absorbance) / a·b

= 0.600 / (5.00×10^3 cm⁻¹ · 1.00 cm)

= 1.20×10^{-4} M.

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b) For first order reaction ⇒ $\ln[X] = \ln[X_0] - kt$

$\therefore \ln[4.00 \times 10^{-5}) = \ln[1.20 \times 10^{-4}] - k\ (35 \text{ minutes})$

$k = 3.14 \times 10^{-2} \text{ min}^{-1}$

c) $\ln(1.50 \times 10^{-5}) = \ln(1.20 \times 10^{-4}) - (3.14 \times 10^{-2})(t)$

$t = 66.2$ minutes.

d) $t_{1/2} = (\ln 2)/k$

$= 22.08$ minutes ≈ 22.1 minutes

e) i) on graph.

ii) The general equation for this graph is:

$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$

$\therefore$ the slope of the graph $= -E_a/R$.

$\therefore$ The activation energy $= -R \cdot$ slope of graph where R is a constant.

$\therefore E_a = -(8.31 \text{ J mol}^{-1} \text{ K}^{-1}) \times (\text{slope of graph})$.

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.

3B 1

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 5.00×10^3 cm^{-1} 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.

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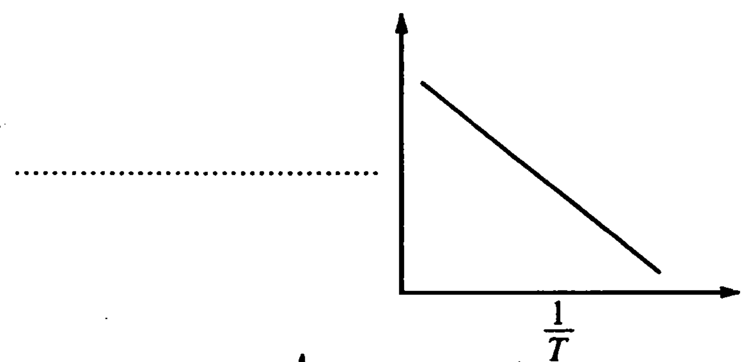
(d) Calculate the half-life of the reaction. Include units with your answer.

(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.



A) $[X]_0 = 1.2 \times 10^{-4}$ M $(4.00 \times 10^{-5} \cdot 3)$

B) $\ln[X]_t - \ln[X]_0 = -kt$

$\ln[4.00 \times 10^{-5}] - \ln[1.2 \times 10^{-4}] = -35\,k$

$k = .0314$ m M^{-1} L^{-1}

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3B2

c) $\ln[1.50\times10^{-5}] - \ln[1.2\times10^{-4}] = -.0314t$

$t = 66.2$

D) $t_{1/2} = -\frac{\ln(\frac{1}{2})}{k}$

$t_{1/2} = -\frac{\ln(\frac{1}{2})}{.0314}$

$t_{1/2} = 22.1$

c) (i) ln k

(ii) The slope of the graph is equal to $\frac{-Ea}{R}$. If one found the slope and multiplied it by a negative R then they would be left with Ea which is the activation energy.

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3C 1

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1.50×10^{-5}	0.075	?

$K = 5.0 \times 10^3$

(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.

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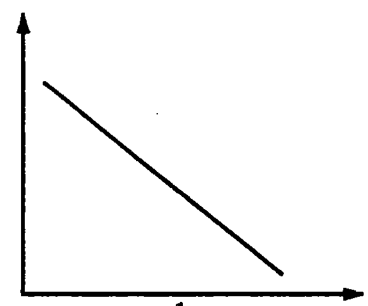
(e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy, E_a, of the reaction.

(i) Label the vertical axis of the graph.

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

(e) i ln[A] ....



(a) $\frac{4.00 \times 10^{-5}}{0.200} = \frac{X}{0.600}$

$[X]_0 = 1.2 \times 10^{-4}\ M$

(b) $\ln(4.00 \times 10^{-5}) = -K(35) + \ln(1.2 \times 10^{-4})$

$K = 3.14 \times 10^{-2}\ min^{-1}$

(d) $\frac{1}{2}$ life $= \frac{\ln 2}{3.14 \times 10^{-2}} = 22.07$ min

(e) ii - $\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ ⇒ use this formula by plugging in points on the graph

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(c) $\ln(1.5 \times 10^{-5}) = -3.14 \times 10^{-2} t + \ln(1.2 \times 10^{-4})$

$= -2.08 = -3.14 \times 10^{-2} t$

$=$ **66.24 minutes**

STOP

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