



AP[®] Chemistry (Operational) 2004 Sample Student Responses

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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.

$A = a \cdot b \cdot C$

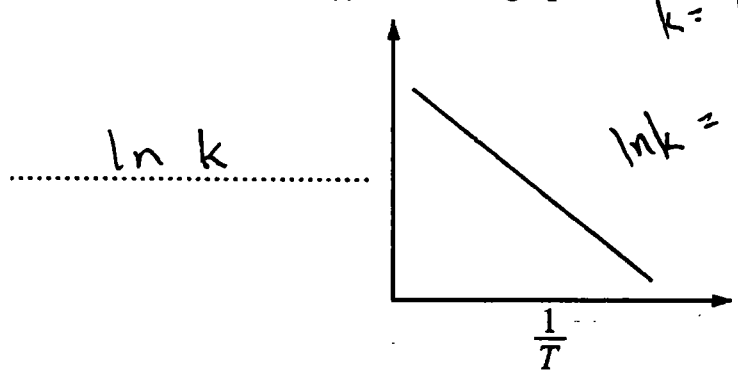
[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?



- (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.

$\frac{\text{mol/L}}{\text{rate}} = k [X] \quad \text{mol}^{-1} \text{min}^{-1}$
 $k =$

- (i) Label the vertical axis of the graph.
- (ii) Explain how to calculate the activation energy from this graph.



$k = A e^{-\frac{E_a}{RT}}$
 $\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right)$
 $\ln k \propto \frac{1}{T}$
 $-\frac{E_a}{R} = m$
 $-E_a = Rm$

a) Absorbance = $a \cdot b \cdot [X]$
 $\therefore [X] = \frac{\text{Absorbance}}{a \cdot b}$
 $= \frac{0.600}{(5.00 \times 10^3 \text{ cm}^{-1} \cdot 1.00 \text{ cm})}$
 $= 1.20 \times 10^{-4} \text{ M.}$

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 3.

$$b) \text{ For first order reaction } \Rightarrow \ln [X] = \ln [X_0] - kt$$

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

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

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

$$t = 66.2 \text{ minutes.}$$

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

$$= 22.08 \text{ minutes} \approx 22.1 \text{ minutes}$$

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 = $-R \cdot \text{slope of graph}$
where R is a constant.

$$\therefore E_a = - (8.315 \text{ mol}^{-1} \text{ K}^{-1}) \times (\text{slope of graph}).$$

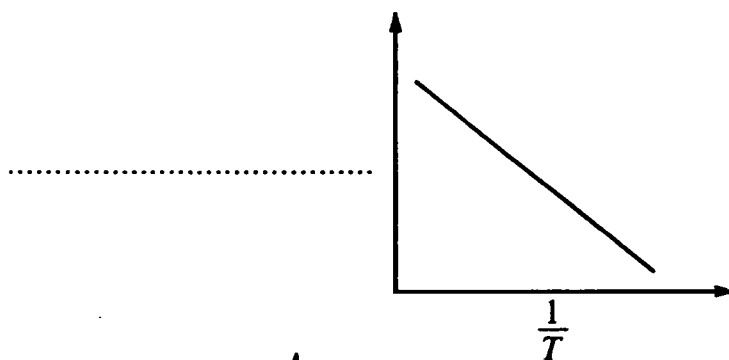
STOP

If you finish before time is called, you may check your work on this part only.
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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.



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

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

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

$k = .0314 \text{ min}^{-1} \text{ M}^{-1} \text{ L}^{-1}$

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$$c) \ln [1.50 \times 10^{-5}] - \ln [1.2 \times 10^{-4}] = -.0314t$$

$$t = 66.2$$

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

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

$$t_{1/2} = 22.1$$

c) (i) $\ln k$

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

STOP

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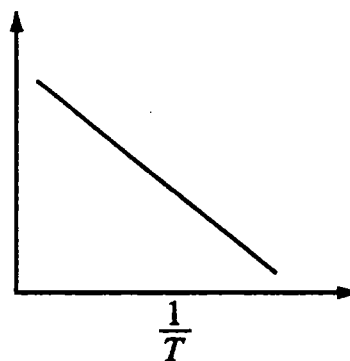
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$k = 5.0 \times 10^3$

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(e) i $\ln[A]$



(a) $4.00 \times 10^{-5} = x$

$\frac{0.200}{0.600} [X]_0 = 1.2 \times 10^{-4} \text{ M}$

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

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

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

(e) ii - $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ \Rightarrow use this formula by plugging in points on the graph

GO ON TO THE NEXT PAGE.

3C2

$$\begin{aligned}
 (c) \ln(1.5 \times 10^{-5}) &= -3.14 \times 10^{-2} t + \ln(1.2 \times 10^{-4}) \\
 &= -2.08 = -3.14 \times 10^{-2} t \\
 &= \boxed{66.24 \text{ minutes}}
 \end{aligned}$$

STOP

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