

1-

$$(a) \text{ Rate} = -\frac{1}{3} \frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{O}_3]}{dt}$$

$$(b) \text{ Rate} = -\frac{d[\text{C}_2\text{H}_6]}{dt} = \frac{d[\text{C}_2\text{H}_4]}{dt} = \frac{d[\text{H}_2]}{dt}$$

$$(c) \text{ Rate} = -\frac{d[\text{ClO}^-]}{dt} = -\frac{d[\text{Br}^-]}{dt} = \frac{d[\text{BrO}^-]}{dt} = \frac{d[\text{Cl}^-]}{dt}$$

$$(d) \text{ Rate} = -\frac{d[(\text{CH}_3)_3\text{CCl}]}{dt} = -\frac{d[\text{H}_2\text{O}]}{dt} = \frac{d[(\text{CH}_3)_3\text{COH}]}{dt} = \frac{d[\text{H}^+]}{dt} = \frac{d[\text{Cl}^-]}{dt}$$

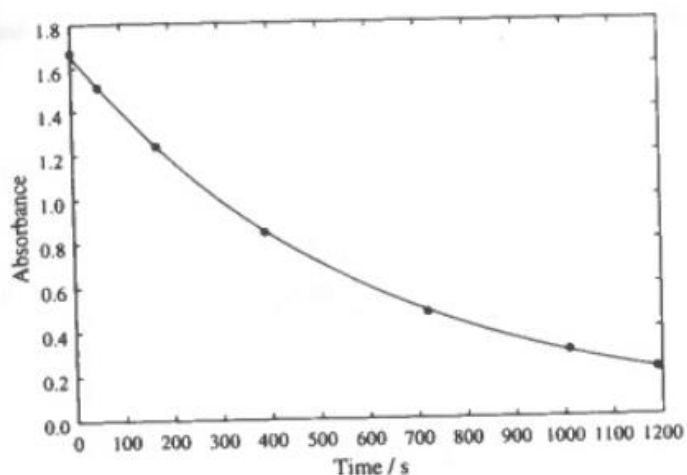
$$(e) \text{ Rate} = -\frac{1}{2} \frac{d[\text{AsH}_3]}{dt} = \frac{1}{2} \frac{d[\text{As}]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

2-

$$\frac{[\text{A}]}{[\text{A}]_0} = e^{-kt}$$

$$k = -\frac{1}{t} \ln \frac{[\text{A}]}{[\text{A}]_0} = -\frac{1}{49 \text{ min}} \ln (1 - 0.345) = 8.6 \times 10^{-3} \text{ min}^{-1}$$

3-



According to the plot, the absorbance decreases from 1.4 to 0.70 as  $t$  goes from 100 s to 505 s. That is, the half-life is 405 s when the absorbance is 1.4. The absorbance decreases from 0.70 to 0.35, over the period  $t$  equals 505 s to 910 s. That is, the half-life is 405 s when the absorbance is 0.70. Since the half-life is independent of reactant concentration, this is a first order reaction.

Let  $[C]$  and  $[C]_0$  be the concentrations of the reactant at time  $t$  and at the beginning of the reaction, respectively; and let  $A$  and  $A_0$  be the absorbance of the reactant at time  $t$  and at the beginning of the reaction, respectively. Since this is a first-order reaction,

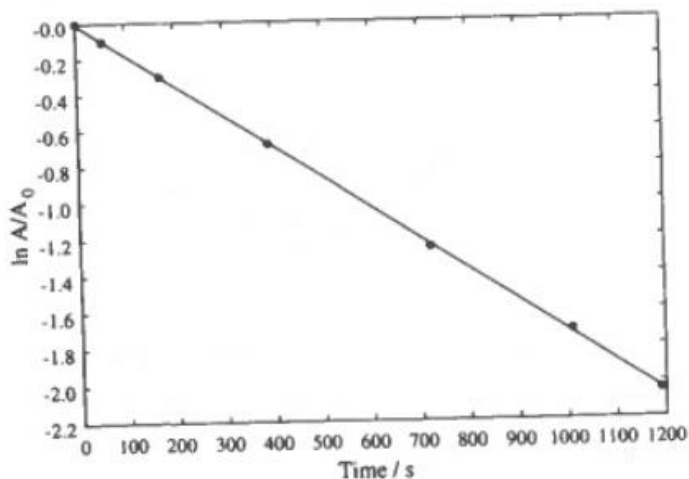
$$[C] = [C]_0 e^{-kt}$$

$$\ln \frac{[C]}{[C]_0} = \ln \frac{A}{A_0} = -kt$$

A plot of  $\ln(A/A_0)$  vs  $t$  will give a straight line with a slope of  $-k$ .

| Time/s       | 0      | 54      | 171     | 390     | 720    | 1010   | 1190   |
|--------------|--------|---------|---------|---------|--------|--------|--------|
| $\ln(A/A_0)$ | 0.0000 | -0.1007 | -0.2977 | -0.6789 | -1.251 | -1.713 | -2.045 |

The equation of the line is  $y = -1.71 \times 10^{-3}x - 6.94 \times 10^{-3}$ . Therefore,  $k = 1.71 \times 10^{-3} \text{ s}^{-1}$ .



4-

The first step involves forward and reverse reactions that are much faster than the second step. The rates of the reaction in the first step are given by

$$\text{Forward rate} = k_1[\text{O}_3]$$

$$\text{Reverse rate} = k_{-1}[\text{O}][\text{O}_2]$$

Assume that these two processes rapidly reach a state of dynamic equilibrium in which the rates of the forward and reverse reactions are equal:

$$k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2]$$

Solving for [O],

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

The rate for the second step gives the rate of reaction,

$$\text{Rate} = k_2[\text{O}][\text{O}_3] = k_2 \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} [\text{O}_3] = \frac{k_1 k_2}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

The rate law shows that higher concentrations of  $\text{O}_2$  will decrease the reaction rate. This is due to the reverse reaction in the first step of the mechanism. If more  $\text{O}_2$  molecules are present, they will serve to scavenge free O atoms and thus slow the disappearance of  $\text{O}_3$ .

5-

Using the Arrhenius equation, with temperatures converted to the kelvin scale,

$$\ln \frac{k_{275.4}}{k_{272.1}} = -\frac{E_a}{R} \left( \frac{1}{275.4 \text{ K}} - \frac{1}{272.1 \text{ K}} \right)$$

$$\ln 2 = -\frac{E_a}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{275.4 \text{ K}} - \frac{1}{272.1 \text{ K}} \right)$$

$$E_a = 1.3 \times 10^5 \text{ J mol}^{-1}$$

(Note that there is a math error in the solution given in the reference that makes the answer there too large by a factor of  $3.3^2$ .) Nevertheless, this is a relatively large  $E_a$ , and temperature will have a large effect on reaction rate. Thus, refrigeration is an essential, effective method of preserving fish and preventing spoilage. Note that the rate of bacterial hydrolysis at room temperature (298 K) is 74 times greater than the rate at 275.4 K.

6-

(a) This reaction occurs in the condensed phase. From Equation 9.43 and the discussion following it, and since  $\Delta U^{\ddagger} \approx \Delta H^{\ddagger}$  in condensed phases,

$$\begin{aligned} E_a &= \Delta U^{\ddagger} + RT \\ &\approx \Delta H^{\ddagger} + RT \end{aligned}$$

or

$$\begin{aligned} \Delta H^{\ddagger} &\approx E_a - RT \\ &= 1.02 \times 10^5 \text{ J mol}^{-1} - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (286 \text{ K}) \\ &= 9.96 \times 10^4 \text{ J mol}^{-1} \end{aligned}$$

From Equation 9.42,

$$A = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R}$$

or

$$\begin{aligned} \Delta S^{\ddagger} &= R \ln \frac{hA}{k_B T} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{(6.626 \times 10^{-34} \text{ J s}) (2.1 \times 10^{16} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) (286 \text{ K})} \\ &= 68 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(b) This is a bimolecular, gas-phase reaction. Using Equation 9.46 with  $\Delta n^\ddagger = -1$ ,

$$E_a = \Delta H^{\circ\ddagger} + 2RT$$

or

$$\begin{aligned}\Delta H^{\circ\ddagger} &= E_a - 2RT \\ &= 5.1 \times 10^4 \text{ J mol}^{-1} - 2 (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (293 \text{ K}) \\ &= 4.6 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

From Equation 9.42,

$$A = \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}/R}$$

or

$$\begin{aligned}\Delta S^{\circ\ddagger} &= R \ln \frac{hA}{k_B T} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{(1 \text{ M}) (6.626 \times 10^{-34} \text{ J s}) (5.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) (293 \text{ K})} \\ &= -96 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

7-

$$\begin{aligned}E &= h\nu = \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s}) (3.00 \times 10^8 \text{ m s}^{-1})}{500 \times 10^{-9} \text{ m}} \\ &= 3.98 \times 10^{-19} \text{ J}\end{aligned}$$

8-

The energy of the photon of wavelength  $\lambda_1$ ,  $E_1$ , equals the sum of the energy of the photon of wavelength  $\lambda_2$ ,  $E_2$ , and the energy of the photon of wavelength  $\lambda_3$ ,  $E_3$ . That is,

$$E_1 = E_2 + E_3$$

$$\frac{hc}{\lambda_1} = \frac{hc}{\lambda_2} + \frac{hc}{\lambda_3}$$

$$\frac{1}{\lambda_1} = \frac{1}{\lambda_2} + \frac{1}{\lambda_3}$$

9-

The energy of a single 600 nm photon is

$$E = h\nu$$

$$= \frac{hc}{\lambda}$$

$$= \frac{(6.626 \times 10^{-34} \text{ J s}) (3.00 \times 10^8 \text{ m s}^{-1})}{600 \times 10^{-9} \text{ m}}$$

$$= 3.313 \times 10^{-19} \text{ J}$$

The number of these photons required to provide  $4.0 \times 10^{-17} \text{ J}$  so that the light can be detected by human eyes is

$$\frac{4.0 \times 10^{-17} \text{ J}}{3.313 \times 10^{-19} \text{ J}} = 1.2 \times 10^2$$

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Let  $m = 1$  and  $n = 2$ .

$$\int_0^L \psi_2 \psi_1 dx = \frac{2}{L} \int_0^L \sin \frac{2\pi x}{L} \sin \frac{\pi x}{L} dx$$

A table of integrals gives, for  $a^2 \neq b^2$ ,

$$\int \sin ax \sin bx dx = \frac{\sin (a - b) x}{2(a - b)} - \frac{\sin (a + b) x}{2(a + b)}$$

Setting  $a = 2\pi/L$  and  $b = \pi/L$ ,

$$\begin{aligned} \int_0^L \psi_2 \psi_1 dx &= \frac{2}{L} \left[ \frac{\sin \frac{\pi x}{L}}{\frac{2\pi}{L}} - \frac{\sin \frac{3\pi x}{L}}{\frac{6\pi}{L}} \right]_0^L \\ &= \frac{2}{L} \left[ \left( \frac{\sin \pi}{\frac{2\pi}{L}} - \frac{\sin 3\pi}{\frac{6\pi}{L}} \right) - \left( \frac{\sin 0}{\frac{2\pi}{L}} - \frac{\sin 0}{\frac{6\pi}{L}} \right) \right] \\ &= \frac{2}{L} [(0 - 0) - (0 - 0)] \\ &= 0 \end{aligned}$$