

# CHAPTER 13

## CHEMICAL KINETICS

**13.1** (a)  $\text{rate}(\text{N}_2) = \text{rate}(\text{H}_2) \times \left( \frac{1 \text{ mol N}_2}{3 \text{ mol H}_2} \right) = \frac{1}{3} \times \text{rate}(\text{H}_2)$

(b)  $\text{rate}(\text{NH}_3) = \text{rate}(\text{H}_2) \times \left( \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} \right) = \frac{2}{3} \times \text{rate}(\text{H}_2)$

(c)  $\text{rate}(\text{NH}_3) = \text{rate}(\text{N}_2) \times \left( \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} \right) = 2 \times \text{rate}(\text{N}_2)$

**13.3** (a) The rate of formation of dichromate ions =

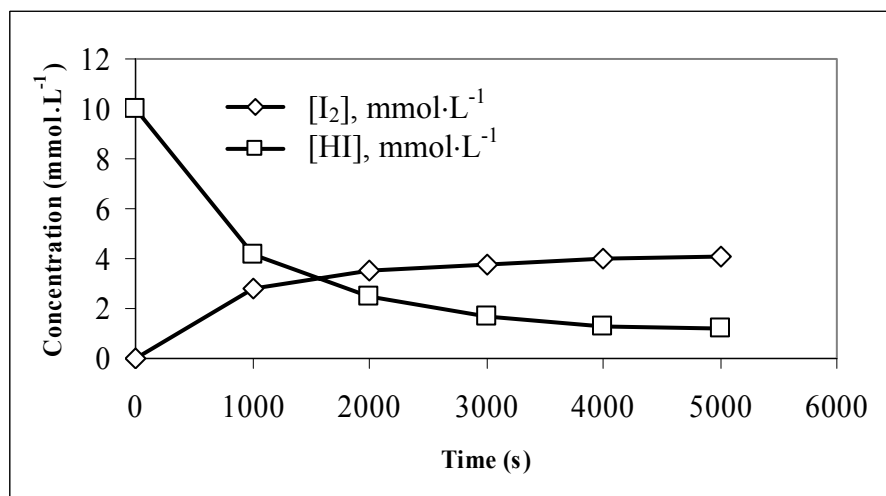
$$\left( \frac{0.14 \text{ mol Cr}_2\text{O}_7^{2-}}{\text{L} \cdot \text{s}} \right) \left( \frac{2 \text{ mol CrO}_4^{2-}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \right) = 0.28 \text{ mol} \cdot \text{L} \cdot \text{s}^{-1} \quad (\text{b})$$

$$0.14 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \div 1 = 0.14 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

**13.5** (a)  $\text{rate of formation of O}_2 = \left( 6.5 \times 10^{-3} \frac{\text{mol NO}_2}{\text{L} \cdot \text{s}} \right) \times \left( \frac{1 \text{ mol O}_2}{2 \text{ mol NO}_2} \right)$   
 $= 3.3 \times 10^{-3} (\text{mol O}_2) \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

(b)  $6.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \div 2 = 3.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

**13.7** (a) and (c)



Note that the curves for the  $[I_2]$  and  $[H_2]$  are identical and only the  $[I_2]$  curve is shown.

(b) The rates at individual points are given by the slopes of the lines tangent to the points in question. If these are determined graphically, there may be some variation from the numbers given below.

time, s    rate,  $\text{mmol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

0        -0.0060

1000    -0.003

2000    -0.000 98

3000    -0.000 61

4000    -0.000 40

5000    -0.000 31

**13.9** For  $A \longrightarrow \text{products}$ , rate =  $(\text{mol } A) \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

(a) rate

$[(\text{mol } A) \cdot \text{L}^{-1} \cdot \text{s}^{-1}] = k_0[A]^0 = k_0$ , so units of  $k_0$  are  $(\text{mol } A) \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

(same as the units for the rate, in this case)

(b) rate

$[(\text{mol } A) \cdot \text{L}^{-1} \cdot \text{s}^{-1}] = k_1[A]$ , so units of  $k_1$  are  $\frac{(\text{mol } A) \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{(\text{mol } A) \cdot \text{L}^{-1}} = \text{s}^{-1}$

(c) rate

$$[(\text{mol A}) \cdot \text{L}^{-1} \cdot \text{s}^{-1}] = k_1 [\text{A}]^2, \text{ so units of } k_1 \text{ are } \frac{(\text{mol A}) \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{[(\text{mol A}) \cdot \text{L}^{-1}]^2}$$
$$= \text{L} \cdot (\text{mol A})^{-1} \cdot \text{s}^{-1}$$

**13.11** From the units of the rate constant,  $k$ , it follows that the reaction is first order, thus  $\text{rate} = k[\text{N}_2\text{O}_5]$ .

$$[\text{N}_2\text{O}_5] = \left( \frac{3.45 \text{ g N}_2\text{O}_5}{0.750 \text{ L}} \right) \left( \frac{1 \text{ mol N}_2\text{O}_5}{108.02 \text{ g N}_2\text{O}_5} \right) = 0.0426 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{rate} = 5.2 \times 10^{-3} \text{ s}^{-1} \times 0.0426 \text{ mol} \cdot \text{L}^{-1} = 2.2 \times 10^{-4} (\text{mol N}_2\text{O}_5) \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

**13.13** From the units of the rate constant, it follows that the reaction is second order; therefore,

$$\text{rate} = k[\text{H}_2][\text{I}_2]$$

$$= (0.063 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) \left( \frac{0.52 \text{ g H}_2}{0.750 \text{ L}} \right) \left( \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \right) \left( \frac{0.19 \text{ g I}_2}{0.750 \text{ L}} \right) \left( \frac{1 \text{ mol I}_2}{253.8 \text{ g I}_2} \right)$$
$$= 2.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

$$(b) \text{ rate}(\text{new}) = k \times 2 \times [\text{H}_2]_{\text{initial}} [\text{I}_2] = 2 \times \text{rate}(\text{initial}), \text{ so, by a factor of 2}$$

**13.15** Because the rate increased in direct proportion to the concentrations of both reactants, the rate is first order in both reactants.

$$\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

**13.17** When the concentration of  $\text{ICl}$  is doubled, the rate doubles (experiments 1 and 2). Therefore, the reaction is first order in  $\text{ICl}$ . When the concentration of  $\text{H}_2$  is tripled, the rate triples (experiments 2 and 3); thus, the reaction is first order in  $\text{H}_2$ .

$$(a) \text{ rate} = k[\text{ICl}][\text{H}_2]$$

$$\begin{aligned} \text{(b)} \quad k &= \left( \frac{22 \times 10^{-7} \text{ mol}}{\text{L} \cdot \text{s}} \right) \left( \frac{\text{L}}{3.0 \times 10^{-3} \text{ mol}} \right) \left( \frac{\text{L}}{4.5 \times 10^{-3} \text{ mol}} \right) \\ &= 0.16 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \text{rate} &= \left( \frac{0.16 \text{ L}}{\text{mol} \cdot \text{s}} \right) \left( \frac{4.7 \times 10^{-3} \text{ mol}}{\text{L}} \right) \left( \frac{2.7 \times 10^{-3} \text{ mol}}{\text{L}} \right) \\ &= 2.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \end{aligned}$$

**13.19** (a) Doubling the concentration of A (experiments 1 and 2) doubles the rate; therefore, the reaction is first order in A. Increasing the concentration of B by the ratio 3.02/1.25 (experiments 2 and 3) increases the rate by  $(3.02/1.25)^2$ ; hence, the reaction is second order in B. Tripling the concentration of C (experiments 3 and 4) increases the rate by  $3^2 = 9$ ; thus, the reaction is second order in C. Therefore,  $\text{rate} = k[\text{A}][\text{B}]^2[\text{C}]^2$ .

(b) overall order = 5

$$\text{(c)} \quad k = \frac{\text{rate}}{[\text{A}][\text{B}]^2[\text{C}]^2}$$

Using the data from experiment 4, we get

$$\begin{aligned} k &= \left( \frac{0.457 \text{ mol}}{\text{L} \cdot \text{s}} \right) \left( \frac{\text{L}}{1.25 \times 10^{-3} \text{ mol}} \right) \left( \frac{\text{L}}{3.02 \times 10^{-3} \text{ mol}} \right)^2 \left( \frac{\text{L}}{3.75 \times 10^{-3} \text{ mol}} \right)^2 \\ &= 2.85 \times 10^{12} \text{ L}^4 \cdot \text{mol}^{-4} \cdot \text{s}^{-1} \end{aligned}$$

From experiment 3, we get

$$\begin{aligned} k &= \left( \frac{5.08 \times 10^{-2} \text{ mol}}{\text{L} \cdot \text{s}} \right) \left( \frac{\text{L}}{1.25 \times 10^{-3} \text{ mol}} \right) \left( \frac{\text{L}}{3.02 \times 10^{-3} \text{ mol}} \right)^2 \\ &\quad \times \left( \frac{\text{L}}{1.25 \times 10^{-3} \text{ mol}} \right)^2 \\ &= 2.85 \times 10^{12} \text{ L}^4 \cdot \text{mol}^{-4} \cdot \text{s}^{-1} \text{ (Checks!)} \end{aligned}$$

$$\begin{aligned}
 \text{(d) rate} &= \left( \frac{2.85 \times 10^{12} \text{ L}^4}{\text{mol}^4 \cdot \text{s}} \right) \left( \frac{3.01 \times 10^{-3} \text{ mol}}{\text{L}} \right) \left( \frac{1.00 \times 10^{-3} \text{ mol}}{\text{L}} \right)^2 \\
 &\quad \times \left( \frac{1.15 \times 10^{-3} \text{ mol}}{\text{L}} \right)^2 \\
 &= 1.13 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}
 \end{aligned}$$

$$\mathbf{13.21} \quad \text{(a)} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1000 \text{ s}} = 6.93 \times 10^{-4} \text{ s}^{-1}$$

$$\text{(b) We use } \ln \left( \frac{[\text{A}]_0}{[\text{A}]_t} \right) = kt \text{ and solve for } k.$$

$$k = \frac{\ln ([\text{A}]_0 / [\text{A}]_t)}{t} = \frac{\ln \left( \frac{0.67 \text{ mol} \cdot \text{L}^{-1}}{0.53 \text{ mol} \cdot \text{L}^{-1}} \right)}{25 \text{ s}} = 9.4 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned}
 \text{(c) } [\text{A}]_t &= \left( \frac{0.153 \text{ mol A}}{\text{L}} \right) - \left[ \left( \frac{2 \text{ mol A}}{1 \text{ mol B}} \right) \left( \frac{0.034 \text{ mol B}}{\text{L}} \right) \right] \\
 &= 0.085 (\text{mol A}) \cdot \text{L}^{-1}
 \end{aligned}$$

$$k = \frac{\ln \left( \frac{0.153 \text{ mol} \cdot \text{L}^{-1}}{0.085 \text{ mol} \cdot \text{L}^{-1}} \right)}{115 \text{ s}} = 5.1 \times 10^{-3} \text{ s}^{-1}$$

$$\mathbf{13.23} \quad \text{(a)} \quad t_{1/2} = \frac{0.693}{k} = \left( \frac{0.693 \text{ s}}{3.7 \times 10^{-5}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{1 \text{ h}}{60 \text{ min}} \right) = 5.2 \text{ h}$$

$$\text{(b) } [\text{A}]_t = [\text{A}]_0 e^{-kt}$$

$$t = 3.5 \text{ h} \times 3600 \text{ s} \cdot \text{h}^{-1} = 1.3 \times 10^4 \text{ s}$$

$$[\text{N}_2\text{O}_5] = 0.0567 \text{ mol} \cdot \text{L}^{-1} \times e^{-(3.7 \times 10^{-5} \text{ s}^{-1})(1.3 \times 10^4 \text{ s})} = 3.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{(c) Solve for } t \text{ from } \ln \left( \frac{[\text{A}]_0}{[\text{A}]_t} \right) = kt, \text{ which gives}$$

$$t = \frac{\ln\left(\frac{[A]_0}{[A]_t}\right)}{k} = \frac{\ln\left(\frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}\right)}{k} = \frac{\ln\left(\frac{0.0567}{0.0135}\right)}{3.7 \times 10^{-5} \text{ s}^{-1}} = 3.9 \times 10^4 \text{ s}$$

$$= (3.9 \times 10^4 \text{ s}) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) = 6.5 \times 10^2 \text{ min}$$

**13.25** (a)  $\frac{[A]}{[A]_0} = \frac{1}{4} = \left(\frac{1}{2}\right)^2$ ; so the time elapsed is 2 half-lives.

$$t = 2 \times 355 \text{ s} = 710 \text{ s}$$

(b) Because 15% is not a multiple of  $\frac{1}{2}$ , we cannot work directly from the half-life. But  $k = 0.693/t_{1/2}$

$$\text{so } k = \frac{0.693}{355 \text{ s}} = 1.95 \times 10^{-3} \text{ s}^{-1}$$

Then [see the solution to Exercise 13.23(c)],

$$t = \frac{\ln\left(\frac{[A]_0}{[A]_t}\right)}{k} = \frac{\ln\left(\frac{1}{0.15}\right)}{1.95 \times 10^{-3} \text{ s}^{-1}} = 9.7 \times 10^2$$

$$(c) \quad t = \frac{\ln \frac{[A]_0}{\frac{1}{9}[A]_0}}{k} = \frac{\ln 9}{1.95 \times 10^{-3} \text{ s}^{-1}} = 1.1 \times 10^3 \text{ s}$$

**13.27** (a)  $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.81 \times 10^{-3} \text{ min}^{-1}} = 247 \text{ min}$

(b) See the solutions to Exercises 13.31(c) and 13.33(c).

$$t = \frac{\ln\left(\frac{[\text{SO}_2\text{Cl}_2]_0}{[\text{SO}_2\text{Cl}_2]_t}\right)}{k} = \frac{\ln 10}{2.81 \times 10^{-3} \text{ min}^{-1}} = 819 \text{ min}$$

(c)  $[A]_t = [A]_0 e^{-kt}$

Because the vessel is sealed, masses and concentrations are proportional, and we write

$$\begin{aligned}
 (\text{mass left})_t &= (\text{mass})_0 e^{-kt} \\
 &= 14.0 \text{ g} \times e^{-(2.81 \times 10^{-3} \text{ min}^{-1} \times 60 \text{ min} \cdot \text{h}^{-1} \times 1.5 \text{ h})} \\
 &= 10.9 \text{ g}
 \end{aligned}$$

Note: Knowledge of the volume of the vessel is not required. However, we could have converted mass to concentration, solved for the new concentration at 1.5 h. and finally converted back to the new (remaining) mass. But this is not necessary

**13.29** (a) We first calculate the concentration of A at 3.0 min.

$$\begin{aligned}
 [A]_t &= [A]_0 - \left( \frac{1 \text{ mol A}}{3 \text{ mol B}} \right) \times [B]_t \\
 &= 0.015 \text{ mol} \cdot \text{L}^{-1} - \left( \frac{1 \text{ mol A}}{3 \text{ mol B}} \right) \times 0.018 (\text{mol B}) \cdot \text{L}^{-1} \\
 &= 0.009 \text{ mol} \cdot \text{L}^{-1}
 \end{aligned}$$

The rate constant is then determined from the first-order integrated rate law.

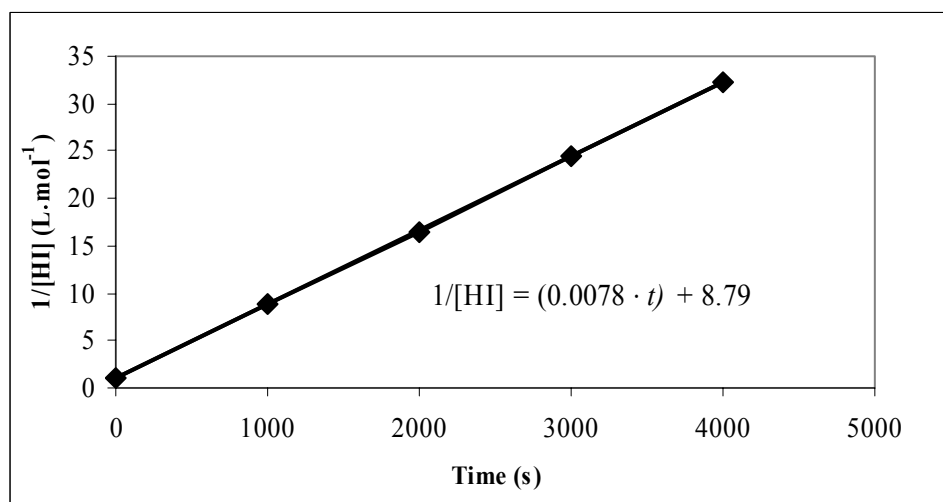
$$k = \frac{\ln \left( \frac{[A]_0}{[A]_t} \right)}{t} = \frac{\ln \left( \frac{0.015}{0.009} \right)}{3.0 \text{ min}} = 0.17 \text{ min}^{-1}$$

$$\begin{aligned}
 \text{(b) } [A]_t &= 0.015 \text{ mol} \cdot \text{L}^{-1} - \left( \frac{1 \text{ mol A}}{3 \text{ mol B}} \right) \times 0.030 (\text{mol B}) \cdot \text{L}^{-1} \\
 &= 0.005 \text{ mol} \cdot \text{L}^{-1}
 \end{aligned}$$

$$t = \frac{\ln \left( \frac{[A]_0}{[A]_t} \right)}{k} = \frac{\ln \left( \frac{0.015}{0.005} \right)}{0.17 \text{ min}^{-1}} = 6.5 \text{ min}$$

$$\text{additional time} = 6.5 \text{ min} - 3.0 \text{ min} = 3.5 \text{ min}$$

**13.31 (a)**



Equation 17.b in the text can be rearranged as

$$\frac{1}{[\text{A}]_t} = \frac{1 + [\text{A}]_0 kt}{[\text{A}]_0} = \frac{1}{[\text{A}]_0} + kt$$

Thus, if the reaction is second order, a plot of  $1/[\text{HI}]$  against time should give a straight line of slope  $k$ .

As can be seen from the graph, the data fit the equation for a second-order reaction quite well. The slope is determined by a least squares fit of the data by the graphing program.

(b) i. The rate constant for the rate law for the loss of HI is simply the slope of the best fit line,  $7.8 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ . ii. Since two moles of HI are consumed per mole of reaction, the rate constant for the unique rate law is half the slope or  $3.9 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

**13.33** It is convenient to obtain an expression for the half-life of a second-order reaction. We work with Eq. 17.b.

$$[\text{A}]_t = \frac{[\text{A}]_0}{1 + [\text{A}]_0 kt} \quad (17.b)$$



$$\frac{[A]_{t_{1/2}}}{[A]_0} = \frac{1}{2} = \frac{1}{1 + [A]_0 k t_{1/2}}$$

Therefore,  $1 + [A]_0 k t_{1/2} = 2$ , or  $[A]_0 k t_{1/2} = 1$ , or

$$t_{1/2} = \frac{1}{k[A]_0} \text{ and } k = \frac{1}{t_{1/2}[A]_0}$$

It is also convenient to rewrite Eq. 17.b to solve for  $t$ . We take reciprocals:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

giving

$$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k}$$

$$(a) \quad k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{(50.5 \text{ s})(0.84 \text{ mol} \cdot \text{L}^{-1})} = 0.024 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$t = \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{k} = \frac{\frac{16}{[A]_0} - \frac{1}{[A]_0}}{k} = \frac{15}{k[A]_0}$$

$$= \frac{15}{(0.024 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(0.84 \text{ mol} \cdot \text{L}^{-1})} = 7.4 \times 10^2 \text{ s}$$

$$(b) \quad t = \frac{\frac{4}{[A]_0} - \frac{1}{[A]_0}}{k} = \frac{3}{k[A]_0}$$

$$= \frac{3}{(0.024 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(0.84 \text{ mol} \cdot \text{L}^{-1})} = 1.5 \times 10^2 \text{ s}$$

$$(c) \quad t = \frac{\frac{5}{[A]_0} - \frac{1}{[A]_0}}{k} = \frac{4}{k[A]_0}$$

$$= \frac{4}{(0.024 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(0.84 \text{ mol} \cdot \text{L}^{-1})} = 2.0 \times 10^2 \text{ s}$$

**13.35** See the solution to Exercise 13.33 for the derivation of the formulas needed here.

$$(a) \quad t = \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{k} = \frac{\frac{1 \text{ L}}{0.080 \text{ mol}} - \frac{1 \text{ L}}{0.10 \text{ mol}}}{0.015 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}} = 1.7 \times 10^2 \text{ min}$$

$$(b) \quad [A] = \frac{0.15 \text{ mol A}}{\text{L}} - \left[ \left( \frac{0.19 \text{ mol B}}{\text{L}} \right) \left( \frac{1 \text{ mol A}}{2 \text{ mol B}} \right) \right]$$

$$= 0.055(\text{mol A}) \cdot \text{L}^{-1} = 0.37[A]_0$$

$$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k}$$

$$= \frac{\frac{1}{0.055 \text{ mol} \cdot \text{L}^{-1}} - \frac{1}{0.15 \text{ mol} \cdot \text{L}^{-1}}}{0.0035 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}}$$

$$= 3.3 \times 10^3 \text{ min}$$

**13.37** (a)  $\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = k[A]$

$$\frac{d[A]}{[A]} = -ak \, dt$$

integrate from  $[A]_0$  at  $t = 0$  to  $[A]_t$  at  $t$ :

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -ak \int_0^t dt$$

$$\ln \frac{[A]_t}{[A]_0} = -akt, \text{ and } [A]_t = [A]_0 \exp(-akt)$$

(b) at  $t_{1/2}$ ,  $[A]_t = \frac{1}{2}[A]_0$ . Therefore:

$$\ln \frac{[A]_0}{[A]_t} = \ln 2 = akt_{1/2}, \text{ and}$$

$$t_{1/2} = \frac{\ln 2}{ak}$$

- 13.39** Given:  $\frac{d[A]}{dt} = -k[A]^3$ , we can derive an expression for the amount of time needed for the initial concentration of A,  $[A]_0$ , to decrease by 1/2. Begin by obtaining the integrated rate law for a third-order reaction by separation of variables:

$$\int_{[A]_0}^{[A]_t} [A]^{-3} d[A] = \int_0^t -k dt = -\frac{1}{2} \left[ [A]_t^{-2} - [A]_0^{-2} \right] = -kt$$

To obtain an expression for the half-life, let  $[A]_t = \frac{1}{2}[A]_0$  and  $t = t_{1/2}$ :

$$-\frac{1}{2} \left[ \left( \frac{1}{2}[A]_0 \right)^{-2} - [A]_0^{-2} \right] = -kt_{1/2}$$

solving for the half-life:

$$t_{1/2} = \frac{3}{2k[A]_0^2}$$

- 13.41** The overall reaction is  $\text{CH}_2\text{RCHCOOH} + \text{HCl} \longrightarrow \text{ClCH}_2\text{CH}_2\text{COOH}$ .

The intermediates include chloride ion,  $\text{CH}_2\text{RCHC}(\text{OH})_2^+$  and  $\text{ClCH}_2\text{CHC}(\text{OH})_2$ .

- 13.43** The first elementary reaction is the rate-controlling step, because it is the slow step. The second elementary reaction is fast and does not affect the overall reaction order, which is second order as a result of the fact that the rate-controlling step is bimolecular.

$$\text{rate} = k[\text{NO}][\text{Br}_2]$$

- 13.45** If mechanism (a) were correct, the rate law would be  $\text{rate} = k_2[\text{NO}_2][\text{CO}]$ .

But this expression does not agree with the experimental result and can be eliminated as a possibility. Mechanism (b) has  $\text{rate} = k_2[\text{NO}_2]^2$  from the slow step. Step 2 does not influence the overall rate, but it is necessary to achieve the correct overall reaction; thus this mechanism agrees with the experimental data  $k = k_2$ . Mechanism

(c) is not correct, which can be seen from the rate expression for the slow

step,  $\text{rate} = k_2[\text{NO}_3][\text{CO}]$ .  $[\text{CO}]$  cannot be eliminated from this expression to yield the experimental result, which does not contain  $[\text{CO}]$ .

- 13.47** (a) True; (b) False. At equilibrium, the *rates* of the forward and reverse reactions are equal, *not the rate constants*. (c) True. (d) False.

Increasing the concentration of a reactant causes the rate to increase by providing more reacting molecules. It does not affect the rate constant of the reaction.

- 13.49** The overall rate of formation of A is  $\text{rate} = -k[\text{A}] + k'[\text{B}]$ . The first term accounts for the forward reaction and is negative as this reaction reduces  $[\text{A}]$ . The second term, which is positive, accounts for the back reaction which increases  $[\text{A}]$ . Given the 1:1 stoichiometry of the reaction, if no B was present at the beginning of the reaction,  $[\text{A}]$  and  $[\text{B}]$  at any time are related by the equation:  $[\text{A}] + [\text{B}] = [\text{A}]_0$  where  $[\text{A}]_0$  is the initial concentration of A. Therefore, the rate law may be written:

$$\frac{d[\text{A}]}{dt} = -k[\text{A}] + k'([\text{A}]_0 - [\text{A}]) = -(k + k')[\text{A}] + k'[\text{A}]_0$$

The solution of this first-order differential equation is:

$$[\text{A}] = \frac{k' + ke^{-(k'+k)t}}{k' + k} [\text{A}]_0$$

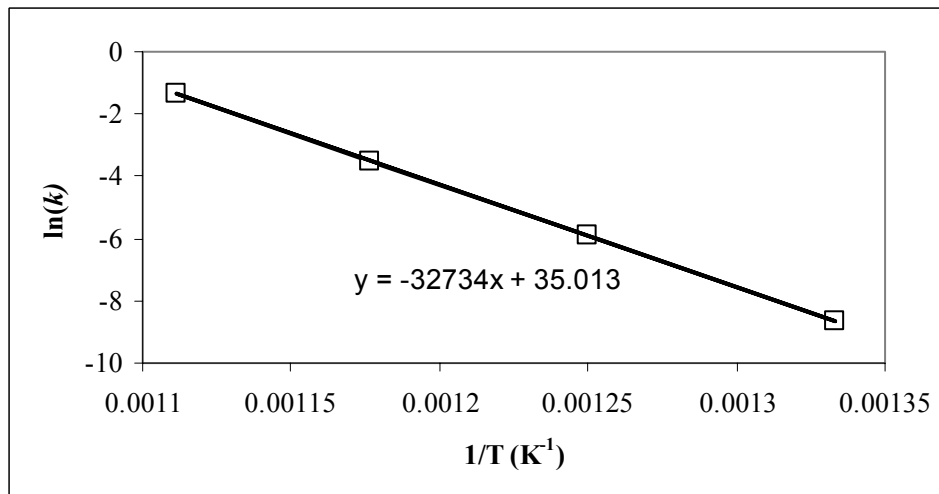
As  $t \rightarrow \infty$  the exponential term in the numerator goes to zero and the concentrations reach their equilibrium values given by:

$$[\text{A}]_{\text{eq}} = \frac{k'[\text{A}]_0}{k' + k} \quad \text{and} \quad [\text{B}]_{\text{eq}} = [\text{A}]_0 - [\text{A}]_{\text{eq}} = \frac{k[\text{A}]_0}{k + k'}$$

taking the ratio of products over reactants we see that:

$$\frac{[\text{B}]_{\text{eq}}}{[\text{A}]_{\text{eq}}} = \frac{k}{k'} = K \quad \text{where } K \text{ is the equilibrium constant for the reaction.}$$

13.51



(a) Given the Arrhenius equation,  $\ln k = \ln A - E_a / RT$ , we see that the slope of the best fit line to the data ( $-3.26 \times 10^4 \text{ K}$ ) is  $\tilde{E}_a / R$  and the y-intercept (35.0) is  $\ln A$ . Therefore,

$$E_a = (3.26 \times 10^4 \text{ K})(8.31 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 2.71 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}.$$

(b) At 600 °C (or 873 K), the rate constant is:

$$\ln(k) = (-3.27 \times 10^4 \text{ K}) \frac{1}{873 \text{ K}} + 35.0 = -2.46$$

$$k = 0.088$$

13.53 We use  $\ln \left( \frac{k'}{k} \right) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) = \frac{E_a}{R} \left( \frac{T' - T}{TT'} \right)$

$$\begin{aligned} \ln \left( \frac{k'}{k} \right) &= \ln \left( \frac{0.87 \text{ s}^{-1}}{0.76 \text{ s}^{-1}} \right) \\ &= \left( \frac{E_a}{8.31 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) \left( \frac{1030 \text{ K} - 1000 \text{ K}}{1030 \text{ K} \times 1000 \text{ K}} \right) \end{aligned}$$

$$\begin{aligned} E_a &= \frac{(8.31 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1000 \text{ K})(1030 \text{ K})(0.14)}{30 \text{ K}} \\ &= 4.0 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

13.55 We use  $\ln \left( \frac{k'}{k} \right) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) = \frac{E_a}{R} \left( \frac{T' - T}{TT'} \right)$

$k'$  = rate constant at 700°C,  $T' = (700 + 273) \text{ K} = 973 \text{ K}$

$$\ln \left( \frac{k'}{k} \right) = \left( \frac{315 \text{ kJ} \cdot \text{mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1}} \right) \left( \frac{973 \text{ K} - 1073 \text{ K}}{973 \text{ K} \times 1073 \text{ K}} \right)$$

$$= -3.63; \quad \frac{k'}{k} = 0.026$$

$$k' = 0.026 \times 9.7 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} = 2.5 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$\mathbf{13.57} \quad \ln \left( \frac{k'}{k} \right) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) = \frac{E_a}{R} \left( \frac{T' - T}{TT'} \right)$$

$$= \left( \frac{103 \text{ kJ} \cdot \text{mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) \left( \frac{323 \text{ K} - 318 \text{ K}}{318 \text{ K} \times 323 \text{ K}} \right) = 0.60$$

$$\frac{k'}{k} = 1.8$$

$$k' = 1.8 \times 5.1 \times 10^{-4} \text{ s}^{-1} = 9.2 \times 10^{-4} \text{ s}^{-1}$$

- 13.59** (a) The equilibrium constant will be given by the ratio of the rate constant of the forward reaction to the rate constant of the reverse reaction:

$$K = \frac{k}{k'} = \frac{265 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}}{392 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}} = 0.676$$

- (b) The reaction profile corresponds to a plot similar to that shown in Fig. 13.31a. The reaction is endothermic—the reverse reaction has a lower activation barrier than the forward reaction.

- (c) Raising the temperature will increase the rate constant of the reaction with the higher activation barrier more than it will the rate constant of the reaction with the lower energy barrier. We expect the rate of the forward reaction to go up substantially more than for the reverse reaction in this case.  $k$  will increase more than  $k'$  and consequently the equilibrium constant  $K$  will increase. This is consistent with Le Chatelier's principle.

**13.61** (a) cat = catalyzed, uncat = uncatalyzed  $E_{\text{a,cat}} = \frac{75}{125} E_{\text{a,uncat}} = 0.60 E_{\text{a,uncat}}$

$$\frac{\text{rate(cat)}}{\text{rate(uncat)}} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{\text{a,cat}}/RT}}{Ae^{-E_{\text{a}}/RT}} = \frac{e^{-(0.40)E_{\text{a}}/RT}}{e^{-E_{\text{a}}/RT}} = e^{(0.40)E_{\text{a}}/RT}$$

$$e^{[(0.40)(125 \text{ kJ} \cdot \text{mol}^{-1}) / (8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 289 \text{ K})]} = 6 \times 10^8$$

(b) The last step of the calculation in (a) is repeated with  $T = 350 \text{ K}$ .

$$e^{[(0.40)(125 \text{ kJ} \cdot \text{mol}^{-1}) / (8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 350 \text{ K})]} = 3 \times 10^7$$

The rate enhancement is lower at higher temperatures.

### 13.63 cat = catalyzed

$$\frac{\text{rate(cat)}}{\text{rate(uncat)}} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = 1000 = \frac{Ae^{-E_{\text{a,cat}}/RT}}{Ae^{-E_{\text{a}}/RT}} = \frac{e^{-E_{\text{a,cat}}/RT}}{e^{-E_{\text{a}}/RT}}$$

$\ln 1000$

$$\begin{aligned} E_{\text{a,cat}} &= E_{\text{a}} - RT \ln 1000 \\ &= 98 \text{ kJ} \cdot \text{mol}^{-1} - (8.31 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 1000) \\ &= 81 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

**13.65** The overall reaction is  $\text{RCN} + \text{H}_2\text{O} \longrightarrow \text{RC(RO)NH}_2$ . The intermediates include

The hydroxide ion serves as a catalyst for the reaction.

- 13.67** (a) False. A catalyst increases the rate of both the forward and reverse reactions by providing a completely different pathway. (b) True, although a catalyst may be poisoned and lose activity. (c) False. There is a completely different pathway provided for the reaction in the presence of a catalyst. (d) False. The position of the equilibrium is unaffected by the presence of a catalyst.

**13.69** (a) To obtain the Michaelis-Menten rate equation, we will begin by employing the steady-state approximation, setting the rate of change in the concentration of the ES intermediate equal to zero:

$$\frac{d[ES]}{dt} = k_1[E][S] - k_1'[ES] - k_2[ES] = 0.$$

rearranging:

$$[E][S] = \frac{k_2 + k_1'}{k_1}[ES] = k_m[ES]$$

The total bound and unbound enzyme concentration,  $[E]_0$ , is given by:

$$[E]_0 = [E] + [ES], \text{ and, therefore,}$$

$$[E] = [ES] - [E]_0$$

Substituting this expression for  $[E]$  into the equation above we obtain:

$$([ES] - [E]_0)[S] = k_m[ES].$$

Rearranging to obtain  $[ES]$ :

$$[ES] = \frac{[E]_0[S]}{k_m + [S]}$$

From the mechanism, the rate of appearance of the product is given by:

rate =  $k_2[ES]$ . Substituting the equation above for  $[ES]$  one obtains:

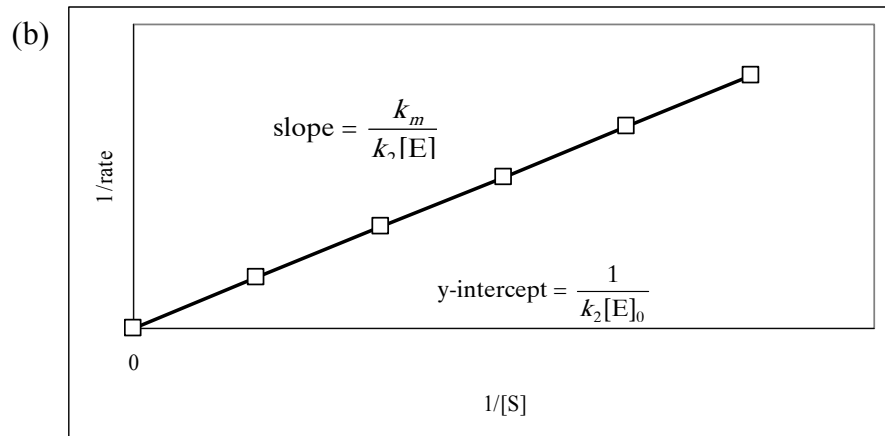
$$\text{rate} = \frac{k_2[E]_0[S]}{k_m + [S]}, \text{ the Michaelis-Menten rate equation, which can be}$$

$$\text{rearranged to obtain: } \frac{1}{\text{rate}} = \frac{k_m}{k_2[E]_0[S]} + \frac{1}{k_2[E]_0}.$$

If one plots  $\frac{1}{\text{rate}}$  vs.  $\frac{1}{[S]}$  the slope will be  $\frac{k_m}{k_2[E]_0}$  and the y-intercept

will be  $\frac{1}{k_2[E]_0}$ .





**13.71** (a) The easiest way to solve this problem is to set up a system of simultaneous equations.

$[\text{H}_2\text{SeO}_3]$	$[\text{I}^-]$	$[\text{H}^+]$	Rate, $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
0.020	0.020	0.010	$8.0 \times 10^{-6}$
0.020	0.010	0.020	$4.0 \times 10^{-6}$
0.020	0.030	0.030	$2.4 \times 10^{-4}$
0.010	0.020	0.020	$1.6 \times 10^{-5}$

We have the following general relationship:

$\text{rate} = k[\text{H}_2\text{SeO}_3]^x [\text{I}^-]^y [\text{H}^+]^z$ , which can be rewritten for ease of computation as

$$\ln(\text{rate}) = \ln k + x \ln [\text{H}_2\text{SeO}_3] + y \ln [\text{I}^-] + z \ln [\text{H}^+]$$

Using the data above, we can create four equations, which should be enough to solve the system of four unknown variables:

$$\ln(8.0 \times 10^{-6}) = \ln k + x \ln 0.020 + y \ln 0.020 + z \ln 0.010$$

$$\ln(4.0 \times 10^{-6}) = \ln k + x \ln 0.020 + y \ln 0.010 + z \ln 0.020$$

$$\ln(2.4 \times 10^{-4}) = \ln k + x \ln 0.020 + y \ln 0.030 + z \ln 0.030$$

$$\ln(1.6 \times 10^{-5}) = \ln k + x \ln 0.010 + y \ln 0.020 + z \ln 0.020$$

which give, upon calculating the numerical logarithms:

$$-11.74 = \ln k - 3.91 x - 3.91 y - 4.60 z \quad (1)$$

$$-12.40 = \ln k - 3.91 x - 4.60 y - 3.91 z \quad (2)$$

$$-8.33 = \ln k - 3.91 x - 3.51 y - 3.51 z \quad (3)$$

$$-11.04 = \ln k - 4.60 x - 3.91 y - 3.91 z \quad (4)$$

Solving this set of simultaneous equations and rounding the  $x$ ,  $y$ , and  $z$  answers to the nearest whole number gives  $x = 1$ ,  $y = 3$ , and  $z = 2$ , with  $k = 5.0 \times 10^5 \text{ L}^5 \cdot \text{mol}^{-5} \cdot \text{s}^{-1}$ .

(b) With

$$[\text{H}_2\text{SeO}_3] = 0.030 \text{ mol} \cdot \text{L}^{-1}, [\text{I}^-] = 0.025 \text{ mol} \cdot \text{L}^{-1} \text{ and } [\text{H}^+] = 0.015 \text{ mol} \cdot \text{L}^{-1},$$

$$\begin{aligned} \text{rate} &= (5.0 \times 10^5 \text{ L}^5 \cdot \text{mol}^{-5} \cdot \text{s}^{-1})(0.030 \text{ mol} \cdot \text{L}^{-1})^1 (0.025 \text{ mol} \cdot \text{L}^{-1})^3 \\ &\quad \times (0.015 \text{ mol} \cdot \text{L}^{-1})^2 \end{aligned}$$

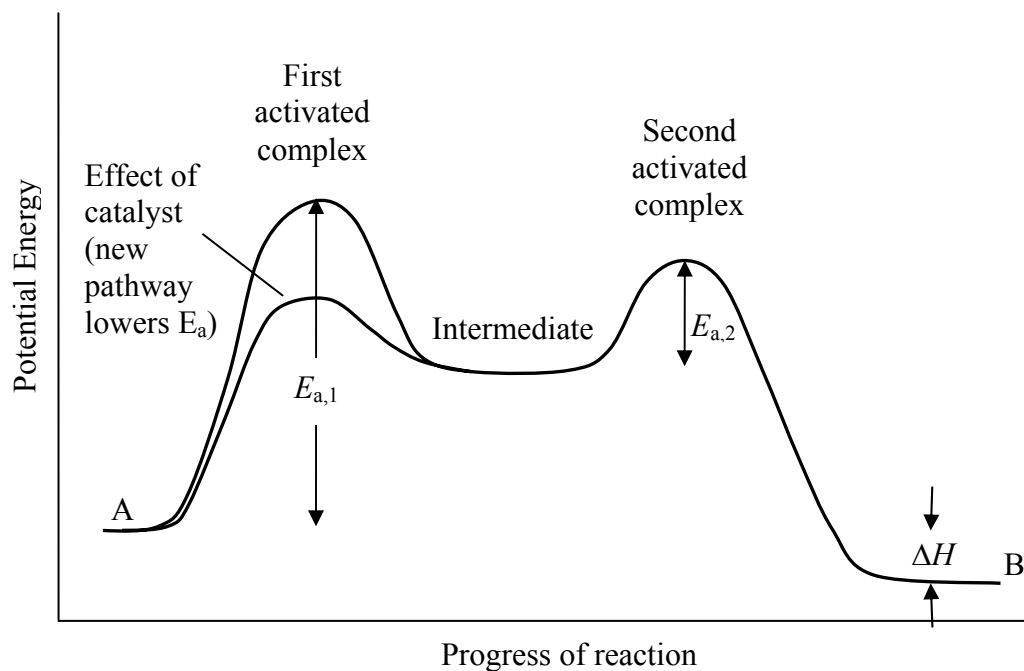
$$\text{rate} = 5.3 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

$$\begin{aligned} \mathbf{13.73} \quad (\text{a}) \quad k &= \frac{\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0}}{t} = \frac{\frac{1}{0.0050 \text{ mol} \cdot \text{L}^{-1}} - \frac{1}{0.040 \text{ mol} \cdot \text{L}^{-1}}}{12 \text{ h}} \\ &= 15 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1} \end{aligned}$$

$$\begin{aligned} (\text{b}) \quad [\text{EX}_2] &= 0.040 \frac{\text{mol EX}_2}{\text{L}} - \left( 0.070 \frac{\text{mol X}}{\text{L}} \right) \left( \frac{1 \text{ mol EX}_2}{2 \text{ mol X}} \right) \\ &= 0.005 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

$$\begin{aligned} k &= \frac{\frac{1}{[\text{EX}_2]_t} - \frac{1}{[\text{EX}_2]_0}}{t} = \frac{\frac{1}{0.005 \text{ mol} \cdot \text{L}^{-1}} - \frac{1}{0.040 \text{ mol} \cdot \text{L}^{-1}}}{15 \text{ h}} \\ &= 10 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1} \quad (1 \text{ sf}) \end{aligned}$$

13.75



13.77  $x$  = amount of original sample = 25.0 mg

$n$  = number of half-lives

$$\left(\frac{1}{2}\right)^n \times x = \text{amount remaining}$$

$$\frac{10.9}{12.3} = 0.886 \text{ half-lives}$$

$$\left(\frac{1}{2}\right)^{0.886} \times 25.0 \text{ mg} = 13.5 \text{ mg}$$

13.79 The anticipated rate for mechanism (i) is:  $\text{rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ , while the expected rate for mechanism (ii) is:  $\text{rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$ . The rate for mechanism (ii) will be pseudo-first-order in dilute solutions of sucrose because the concentration of water will not change. Therefore, in dilute solutions kinetic data can not be used to distinguish between the two mechanisms. However, in a highly concentrated solution of sucrose, the concentration of water will change during the course of the reaction. As a

result, if mechanism (ii) is correct the kinetics will display a first-order dependence on the concentration of  $\text{H}_2\text{O}$  while mechanism (i) predicts that the rate of the reaction is independent of  $[\text{H}_2\text{O}]$ .

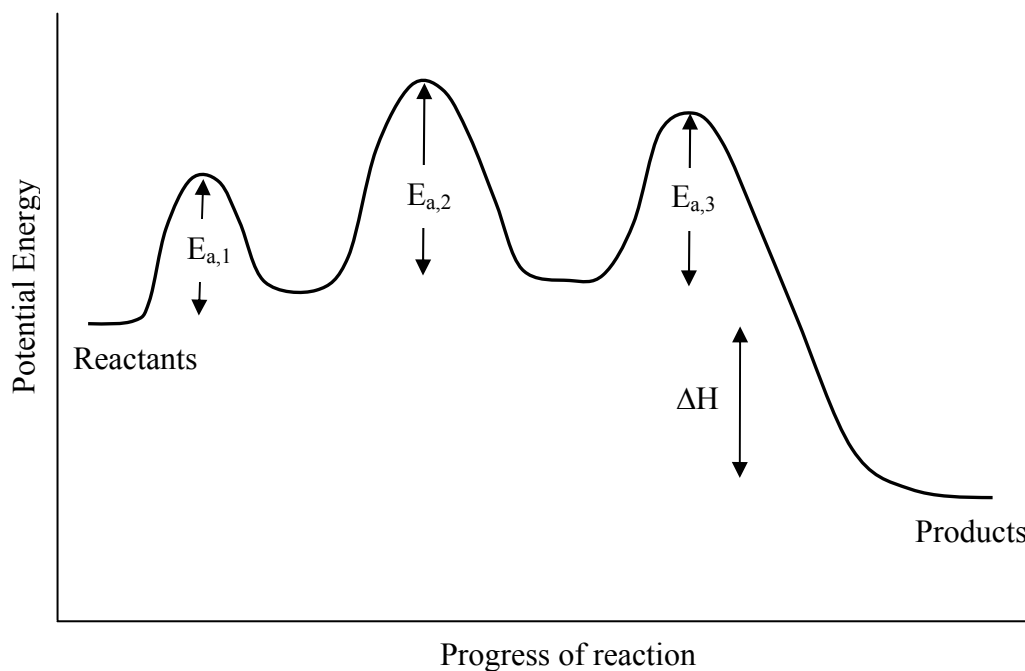
- 13.81** (a) The objective is to reproduce the observed rate law. If step 2 is the slow step, if step 1 is a rapid equilibrium, and if step 3 is fast also, then our proposed rate law will be  $\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$ . Consider the equilibrium of Step 1:  $k_1[\text{NO}]^2 = k_1'[\text{N}_2\text{O}_2]$

$$[\text{N}_2\text{O}_2] = \frac{k}{k_1'}[\text{NO}]^2 \text{ Substituting in our proposed rate law, we have}$$

$$\text{rate} = k_2 \left( \frac{k_1}{k_1'} \right) [\text{NO}]^2 [\text{H}_2] = k[\text{NO}]^2 [\text{H}_2] \text{ where } k = k_2 \left( \frac{k_1}{k_1'} \right)$$

The assumptions made above reproduce the observed rate law; therefore, step 2 is the slow step.

(b)



Note: The dips that represent the formation of the intermediate  $\text{N}_2\text{O}_2$  and  $\text{N}_2\text{O}$  will not be at the same energy, but we have no information to determine which should be lower.

$$13.83 \quad \frac{\text{rate at } 28^\circ\text{C}}{\text{rate at } 5^\circ\text{C}} = \frac{k'}{k} = \frac{t}{t'} = \frac{48 \text{ h}}{4 \text{ h}}$$

We use  $\ln\left(\frac{k'}{k}\right) = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$  and solve for  $E_a$ .

$$E_a = \frac{R \ln\left(\frac{k'}{k}\right)}{\left(\frac{1}{T} - \frac{1}{T'}\right)} = \frac{(8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln\left(\frac{48}{4}\right)}{\left(\frac{1}{278 \text{ K}} - \frac{1}{301 \text{ K}}\right)} = 75 \text{ kJ} \cdot \text{mol}^{-1}$$

- 13.85 (a) To obtain the Michaelis-Menten rate equation assuming a pre-equilibrium between the bound and unbound states of the substrate we begin with the expression for the equilibrium constant of the fast equilibrium between the bound and unbound substrate:

$$K = \frac{[\text{ES}]}{[\text{E}][\text{S}]}, \quad \text{solving for } [\text{ES}] \text{ we obtain: } [\text{ES}] = K[\text{E}][\text{S}]$$

as before in problem 13.69, the total bound and unbound enzyme concentration,  $[\text{E}]_0$ , is given by:

$$[\text{E}]_0 = [\text{E}] + [\text{ES}], \text{ and, therefore,}$$

$$[\text{E}] = [\text{E}]_0 - [\text{ES}]$$

Substituting this expression for  $[\text{E}]$  into the equation above we obtain:

$$K([\text{E}]_0 - [\text{ES}])[\text{S}] = [\text{ES}].$$

Rearranging to obtain  $[\text{ES}]$ :

$$[\text{ES}] = \frac{K[\text{E}]_0[\text{S}]}{1 + K[\text{S}]} = \frac{[\text{E}]_0[\text{S}]}{K^{-1} + [\text{S}]}$$

From the mechanism, the rate of appearance of the product is given by:

rate =  $k_2[\text{ES}]$ . Substituting the equation above for  $[\text{ES}]$  one obtains:

$$\text{rate} = \frac{k_2[\text{E}]_0[\text{S}]}{K^{-1} + [\text{S}]}, \text{ the Michaelis-Menten rate equation.}$$

- 13.87 (a)  $\text{ClO}$  is the reaction intermediate;  $\text{Cl}$  is the catalyst.

- (b) Cl, ClO, O, O<sub>2</sub>
- (c) Step 1 is initiating; step 2 is propagating.
- (d)  $\text{Cl} + \text{Cl} \longrightarrow \text{Cl}_2$

**13.89** For a third-order reaction,

$$t_{1/2} \propto \frac{1}{[\text{A}_0]^2} \text{ or } t_{1/2} = \frac{\text{constant}}{[\text{A}_0]^2}$$

(a) The time necessary for the concentration to fall to one-half of the initial concentration is one half-life:

$$\text{first half-life} = t_1 = t_{1/2} = \frac{\text{constant}}{[\text{A}_0]^2}$$

(b) This time,  $t_{1/4}$ , is two half-lives, but because of different starting concentrations, the half-lives are not the same:

$$\text{second half-life} = t_2 = \frac{\text{constant}}{(\frac{1}{2}[\text{A}_0])^2} = \frac{4(\text{constant})}{[\text{A}_0]^2} = 4t_1$$

$$\text{total time} = t_1 + t_2 = t_1 + 4t_1 = 5t_1 = t_{1/4}$$

(c) This time,  $t_{1/16}$ , is four half-lives; again, the half-lives are not the same:

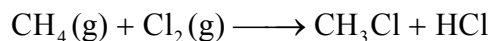
$$\text{third half-life} = t_3 = \frac{\text{constant}}{(\frac{1}{4}[\text{A}_0])^2} = \frac{16(\text{constant})}{[\text{A}_0]^2} = 16t_1$$

$$\text{fourth half-life} = t_4 = \frac{\text{constant}}{(\frac{1}{8}[\text{A}_0])^2} = \frac{64(\text{constant})}{[\text{A}_0]^2} = 64t_1$$

$$\text{total time} = t_1 + t_2 + t_3 + t_4 = t_1 + 4t_1 + 16t_1 + 64t_1 = 85t_1 = t_{1/16}$$

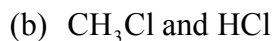
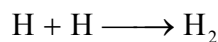
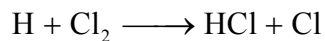
If  $t_1$  is known, the times  $t_{1/4}$  and  $t_{1/16}$  can be calculated easily.

**13.91** By analogy with the reaction in Exercise 13.82, the overall reaction here is



(a) Initiation:  $\text{Cl}_2 \longrightarrow 2 \text{Cl}$

Propagation:  $\text{Cl} + \text{CH}_4 \longrightarrow \text{CH}_3\text{Cl} + \text{H}$



**13.93** The strategy for working this problem is to obtain the equilibrium constants for the reaction at two or more temperatures and then use those values to calculate  $\Delta H^\circ_{\text{r}}$  and  $\Delta S^\circ_{\text{r}}$ . From Table 13.1 we can obtain  $K$  values at 4 temperatures:

$$K = \frac{k}{k'}$$

$$K_{500} = \frac{6.4 \times 10^{-9} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}{4.3 \times 10^{-7} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 0.015$$

$$K_{600} = \frac{9.7 \times 10^{-6} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}{4.4 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 0.022$$

$$K_{700} = \frac{1.8 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}{6.3 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 0.028$$

$$K_{700} = \frac{9.7 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}{2.6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 0.037$$

We can choose to calculate the desired quantities from any two of these points, or we can plot the data and determine the values from the slope and intercept of the graph:

$$\ln K = -\frac{\Delta H^\circ_{\text{r}}}{R} \left( \frac{1}{T_1} \right) + \frac{\Delta S^\circ_{\text{r}}}{R}$$

The plot should be  $\ln K$  versus  $\frac{1}{T}$ . The slope will be  $-\frac{\Delta H^\circ_{\text{r}}}{R}$  and the

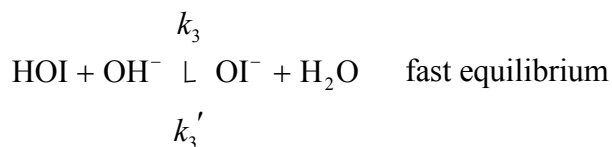
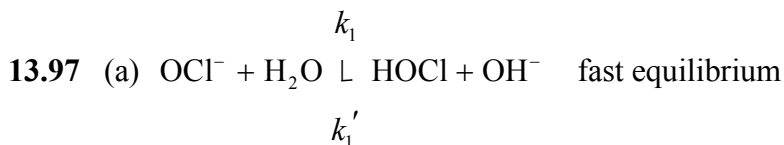
intercept will be  $\frac{\Delta S^\circ_{\text{r}}}{R}$ .

$T(\text{K})$	$\frac{1}{T}(\text{K}^{-1})$	$K$	$\ln K$
500	0.0200	0.015	-4.20
600	0.001 67	0.022	-3.82
700	0.001 43	0.028	-3.58
800	0.001 25	0.037	-3.30

$$-\frac{\Delta H^\circ_r}{R} = -1177, \Delta H^\circ_r = 9.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\frac{\Delta S^\circ_r}{R} = -1.86, \Delta S^\circ_r = -15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

**13.95** In order for the reaction to be catalyzed heterogeneously, the reacting species must attach themselves to the surface of the catalyst. The concentration of the reactants is usually much greater than the number of active sites available on the catalyst so that the rate is determined by the surface area of the catalyst and not by the concentrations or pressures of reactants.



The overall reaction is  $\text{OCl}^- + \text{I}^- \longrightarrow \text{OI}^- + \text{Cl}^-$

(b) The rate law will be based upon the slow step of the reaction:

$$\text{rate} = k_2[\text{HOCl}][\text{I}^-]$$

Even though HOCl is a stable species because it is an intermediate in the reaction as written, technically we should not leave the rate law in this



form. The concentration of HOCl can be expressed in terms of the reactants and products using the fast equilibrium approach:

$$K = \frac{k_1}{k_1'} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

$$[\text{HOCl}] = \frac{k_1}{k_1'} \frac{[\text{OCl}^-]}{[\text{OH}^-]}$$

$$\text{rate} = \frac{k_2 k_1}{k_1'} \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

(c) An examination of the rate law shows that the rate is dependent upon the concentration of  $\text{OH}^-$ , which means that the rate will be dependent upon the pH of the solution.

(d) If the reaction is carried out in an organic solvent, then  $\text{H}_2\text{O}$  is no longer the solvent and its concentration must be included in calculating the equilibrium concentration of HOCl:

$$K = \frac{k_1}{k_1'} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-][\text{H}_2\text{O}]}$$

$$[\text{HOCl}] = \frac{k_1}{k_1'} \frac{[\text{OCl}^-][\text{H}_2\text{O}]}{[\text{OH}^-]}$$

$$\text{rate} = \frac{k_2 k_1}{k_1'} \frac{[\text{OCl}^-][\text{I}^-][\text{H}_2\text{O}]}{[\text{OH}^-]}$$

The rate of reaction will then show a dependence upon the concentration of water, which will be obscured when the reaction is carried out with water as the solvent.

<b>13.99</b>	Concentration ( $\text{mol} \cdot \text{L}^{-1}$ )	$2 \text{ N}_2\text{O}_5$	$\rightleftharpoons$	$4 \text{ NO}_2$	+	$\text{O}_2$
	initial	$P_0$		0		0
	change	$-x$		$+2x$		$+0.5x$
	at time $t$	$P_0 - x$		$2x$		$0.5x$

Therefore,  $P_{\text{total}}$  at time  $t = P_0 + 1.5x$ . This allows calculation of  $x$  at each time, which in turn allows calculation of  $P_{\text{N}_2\text{O}_5} (= P_0 - x)$  at these times.

Converting the units to atmospheres by dividing by

$101.325 \text{ kPa} \cdot \text{atm}^{-1}$  and to  $[\text{N}_2\text{O}_5]$  by dividing by  $RT$  allows us to make the following table:

$t, \text{ min}$	$x, \text{ kPa}$	$P_{\text{N}_2\text{O}_5}, \text{ kPa}$	$P_{\text{N}_2\text{O}_5}, \text{ atm}$	$[\text{N}_2\text{O}_5], \text{ mol} \cdot \text{L}^{-1}$	$\ln [\text{N}_2\text{O}_5]$
0	0	27.3	0.269	0.0100	-4.605
5	10.9	16.4	0.162	$6.01 \times 10^{-3}$	-5.114
10	17.5	9.85	0.0972	$3.61 \times 10^{-3}$	-5.624
15	21.4	5.9	0.058	$2.2 \times 10^{-3}$	-6.12
20	23.8	3.5	0.035	$1.3 \times 10^{-3}$	-6.65
30	26.0	1.3	0.013	$4.8 \times 10^{-4}$	-7.64

The data fit closely to a straight line; therefore, this is a first-order reaction. The rate constant can be obtained from the slope, which is

$$\frac{-4.605 - (-7.64)}{30 \text{ min}} = 0.101 \text{ min}^{-1} = k$$

rate  $= k[\text{N}_2\text{O}_5] = 0.101 \text{ min}^{-1}[\text{N}_2\text{O}_5]$ , which gives the results in the table below.

$t, \text{ min}$	rate, $\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$
0	$1.01 \times 10^{-3}$
5	$6.07 \times 10^{-4}$
10	$3.65 \times 10^{-4}$
15	$2.2 \times 10^{-4}$
20	$1.3 \times 10^{-4}$
30	$4.8 \times 10^{-5}$