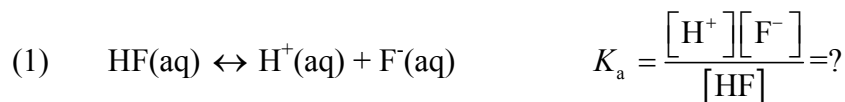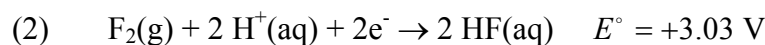$$t = \frac{1.59 \times 10^5 \ \text{C}}{2.0 \ \text{A}} = 7.94 \times 10^4 \ \text{s} \left(\frac{1 \ \text{hour}}{3600 \ \text{s}} \right) = 22 \ \text{hours}$$
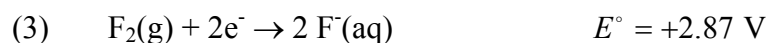
12.112 The reaction of interest is

(1) $\text{HF(aq)} \leftrightarrow \text{H}^+\text{(aq)} + \text{F}^-\text{(aq)}$ $K_a = \dfrac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = ?$

We have

(2) $\text{F}_2\text{(g)} + 2 \ \text{H}^+\text{(aq)} + 2\text{e}^- \rightarrow 2 \ \text{HF(aq)}$ $E° = +3.03 \ \text{V}$

and from Appendix 2B,

(3) $\text{F}_2\text{(g)} + 2\text{e}^- \rightarrow 2 \ \text{F}^-\text{(aq)}$ $E° = +2.87 \ \text{V}$

Since combining reactions $(1/2)(3) - (1/2)(2) = (1)$,

$E_{(1)}° = +2.87 \ \text{V} - 3.03 \ \text{V} = -0.16 \ \text{V}$

$\Delta G° = -nFE° = -RT \ln K$

$K = e^{\frac{nFE°}{RT}} = e^{\frac{(96 \ 485)(-0.16)}{(8.314)(298.15)}} = e^{-6.228} = 2.0 \times 10^{-3}$

(We note that this value for K_a does not match the one given in Table 10.1 on page 376, 3.5×10^{-4}. There may be a mistake in the data given here or the thermodynamic values may have been determined from different experiments.)

CHAPTER 13
CHEMICAL KINETICS

13.2 (a) $\text{rate}(N_2O_5) = -\text{rate}(O_2) \times \left(\dfrac{2 \text{ mol } N_2O_5}{1 \text{ mol } O_2} \right) = -2 \text{ rate}(O_2)$

(b) $\text{rate}(NO_2) = -\text{rate}(N_2O_5) \times \left(\dfrac{4 \text{ mol } NO_2}{2 \text{ mol } N_2O_5} \right) = -2 \text{ rate}(N_2O_5)$

(c) $\text{rate}(NO_2) = \text{rate}(O_2) \times \left(\dfrac{4 \text{ mol } NO_2}{1 \text{ mol } O_2} \right) = 4 \text{ rate}(O_2)$

13.4 (a) rate of change of $[CLO^-] = -\text{rate}(O_2) \times \left(\dfrac{3.6 \text{ mol } Cl^-}{L \cdot \min} \right) \left(\dfrac{3 \text{ mol } ClO^-}{2 \text{ mol } Cl^-} \right)$
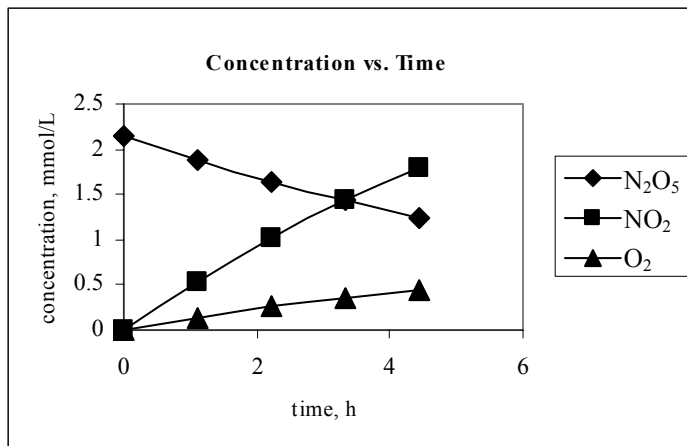
$$= 5.4 \text{ mol} \cdot L^{-1} \cdot \min^{-1}$$

(b) $3.6 \text{ mol} \cdot L^{-1} \cdot \min^{-1} \div 2 = 1.8 \text{ mol} \cdot L^{-1} \cdot \min^{-1}$

13.6 (a) rate of formation of $MnO_4^- = \left(2.0 \text{ mol} \dfrac{MnO_4^{2-}}{L \cdot \min} \right) \left(\dfrac{2 \text{ mol } MnO_4^-}{3 \text{ mol } MnO_4^{2-}} \right)$

$$= 5.4 \text{ mol} \cdot L^{-1} \cdot \min^{-1}$$

(b) rate of reaction of $H^+(aq) = \left(2.0 \text{ mol} \dfrac{MnO_4^{2-}}{L \cdot \min} \right) \left(\dfrac{4 \text{ mol } H^+}{3 \text{ mol } MnO_4^{2-}} \right)$

$$= 2.7 \text{ mol } H^+ \cdot L^{-1} \cdot \min^{-1}$$

(c) rate of reaction of $H^+(aq) = \left(2.0 \text{ mol} \dfrac{MnO_4^{2-}}{L \cdot \min} \right) \left(\dfrac{4 \text{ mol } H^+}{3 \text{ mol } MnO_4^{2-}} \right)$

$$2.7 \text{ mol} \cdot L^{-1} \cdot \min^{-1} \div 3 = 0.67 \text{ mol} \cdot L^{-1} \cdot \min^{-1}$$

13.8 (a) and (c)

Concentration vs. Time

(b) The rates are calculated from the slopes of the lines drawn tangent to the curve at each point. Doing this by hand on the graph leads to a fair amount of error in determination of the slopes. One can also determine the values by taking the derivative of the curve fitted to the data points followed by insertion of the specific time values into the derivative equation. Fitting the data to the function concentration = A·exp(-B·time) the constants A and B are found to be: 2.1514 and 0.1224, respectively. The instantaneous rates are, therefore:

time	rate, $mmol \cdot L^{-1} \cdot h^{-1}$
0	−0.2024
1.11	−0.2092
2.22	−0.2154
3.33	−0.2210
4.44	−0.2260

13.10 (a) rate $(Torr \cdot s^{-1}) = k_o P^o = k_o$

$k_o = Torr \cdot s^{-1}$

(b) rate $(Torr \cdot s^{-1}) = k_1 P$

$k_1 = (Torr \cdot s^{-1})/Torr = s^{-1}$

(c) rate $(Torr \cdot s^{-1}) = k_2 P^2$

$k_2 = (Torr \cdot s^{-1})/(Torr^2) = Torr^{-1} \cdot s \, s^{-1}$

13.12 $\text{rate} = k\left[\text{C}_2\text{H}_6\right] = 5.55 \times 10^{-4}\,\text{s}^{-1}\left(\dfrac{0.250 \text{ g C}_2\text{H}_6}{0.500 \text{ L}}\right)\left(\dfrac{1 \text{ mol C}_2\text{H}_6}{30.07 \text{ g C}_2\text{H}_6}\right)$

$\text{rate} = 9.1 \times 10^{-6}\,\left(\text{mol C}_2\text{H}_6\right)\text{L}^{-1}\cdot\text{s}^{-1}$

13.14   (a) The units of the rate constant indicate that the reaction is second order, thus

$\text{rate} = k\left[\text{NO}_2\right]_0^2 = \left(\dfrac{0.54 \text{ L}}{\text{mol}\cdot\text{s}}\right)\left[\left(\dfrac{0.420 \text{ g}}{0.15 \text{ L}}\right)\left(\dfrac{1 \text{ mol NO}_2}{46.01 \text{ g NO}_2}\right)\right]^2$

$= 2.0 \times 10^{-3}\,\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

(b) The rate increases by a factor of $\left(\dfrac{750}{420}\right)^2 = 3.19$

13.16 $\text{rate} = k[\text{NO}]^a[\text{O}_2]^b$, where the orders a and b are to be determined. When the concentration of NO is doubled the rate increases by a factor of 4, that is

$$2^a = 4, \text{ so } a = 2$$

When both the concentration of NO and O_2 are doubled, the rate increases by a factor of 8, that is

$$2^2 \times 2^b = 8, \text{ so } b = 1$$

Therefore, the rate law is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

13.18   (a) and (b) $\text{rate} = k[\text{NO}_2]_0[\text{O}_3]_0$, because increasing the concentration of either reactant by a factor while holding the other concentration constant increases the rate by that same factor; the reaction is first order in each reactant and second order overall.

$k = \dfrac{\text{rate}}{[\text{NO}_2]_0[\text{O}_3]_0}$

(c) $= \left(\dfrac{11.4 \text{ mmol}}{\text{L}\cdot\text{s}}\right)\left(\dfrac{\text{L}}{0.38 \times 10^{-3} \text{ mmol}}\right)\left(\dfrac{\text{L}}{0.70 \times 10^{-3} \text{ mmol}}\right)$

$= 0.38 \times 10^{-3}\,\text{L}\cdot\text{mmol}^{-1}\cdot\text{s}^{-1}$

(d) $\text{rate} = \left(\dfrac{4.3 \times 10^{-7} \text{ L}}{\text{mmol} \cdot \text{s}} \right) \left(\dfrac{0.66 \times 10^{-3} \text{ mmol}}{\text{L}} \right) \left(\dfrac{0.18 \times 10^{-3} \text{ mmol}}{\text{L}} \right)$

$= 5.1 \text{ mmol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

13.20 (a) $\text{rate} = k[\text{A}]_0^a[\text{B}]_0^b[\text{C}]_0^c$

$\dfrac{\text{rate (exp 1)}}{\text{rate (exp 2)}} = \dfrac{[A]_0^a \text{ (exp 1)}}{[A]_0^a \text{ (exp 2)}}$

$\left(\dfrac{3.7}{0.66} \right) = \left(\dfrac{2.06}{0.87} \right)^a$

$5.6 = 2.37^a$

by inspection, $a = 2$.

$\dfrac{\text{rate (exp 4)}}{\text{rate (exp 3)}} = \dfrac{[A]_0^2[C]_0^c \text{ (exp 4)}}{[A]_0^2[C]_0^c \text{ (exp 3)}}$

$\left(\dfrac{0.072}{0.013} \right) = \left(\dfrac{1.00}{0.50} \right)^2 \left(\dfrac{1.00}{0.50} \right)^c$

$5.5 = 4 \times 2.0^c \quad \text{or} \quad 2.0^c = 1.4$

$c \log 2 = 0.15$

$c = 0.48 \cong 0.5$

$\dfrac{\text{rate (exp 2)}}{\text{rate (exp 3)}} = \dfrac{[A]_0^2[B]_0^b[C]_0^{0.5} \text{ (exp 2)}}{[A]_0^2[B]_0^b[C]_0^{0.5} \text{ (exp 3)}}$

$\left(\dfrac{0.66}{0.013} \right) = \left(\dfrac{0.87}{0.50} \right)^2 \left(\dfrac{3.05}{0.50} \right)^b \left(\dfrac{4.00}{0.50} \right)^{0.5}$

$51 = 8.6 \times 6.1^b \quad \text{or} \quad 6.1^b = 5.9$

$b \log 6.1 = 0.77$

$b = 0.99 \cong 1$

Therefore, $\text{rate} = k[\text{A}]_0^2[\text{B}]_0[\text{C}]_0^{0.5}$

(b) $\text{order} = 2 + 1 + \frac{1}{2} = 3.5$

(c) $k = \dfrac{\text{rate}}{[A]_0^2 [B]_0 [C]_0^{0.5}}$

Using data from experiment 1

$$k = \dfrac{3.7 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{\left(2.06 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}\right)^2 \left(3.05 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}\right)\left(4.00 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}\right)^{0.5}}$$

$$k = 4.5 \times 10^6\ \left(\text{L} \cdot \text{mol}^{-1}\right)^{5/2} \cdot \text{s}^{-1}$$

13.22 (a) $k = \dfrac{\ln\left(\dfrac{[A]_0}{[A]_t}\right)}{t} = \dfrac{\ln\left(\dfrac{[A]_0}{\frac{1}{4}[A]_0}\right)}{t} = \dfrac{\ln 4}{38\ \text{min}} = 0.036\ \text{min}^{-1}$

(b) $[A]_t = 0.039(\text{mol A}) \cdot \text{L}^{-1} - \left(\dfrac{0.0095\ \text{mol B}}{1\ \text{L}}\right)\left(\dfrac{2\ \text{mol A}}{1\ \text{mol B}}\right)$

$\qquad = 0.020\ \text{mol} \cdot \text{L}^{-1}$

$k = \dfrac{\ln\left(\dfrac{0.039\ \text{mol} \cdot \text{L}^{-1}}{0.020\ \text{mol} \cdot \text{L}^{-1}}\right)}{75\ \text{s}} = 8.9 \times 10^{-3}\ \text{s}^{-1}$

(c) $[A]_t = 0.040(\text{mol A}) \cdot \text{L}^{-1} - \left(\dfrac{0.030\ \text{mol B}}{1\ \text{L}}\right)\left(\dfrac{2\ \text{mol A}}{3\ \text{mol B}}\right)$

$\qquad = 0.020\ \text{mol} \cdot \text{L}^{-1}$

$k = \dfrac{\ln\left(\dfrac{0.040\ \text{mol} \cdot \text{L}^{-1}}{0.020\ \text{mol} \cdot \text{L}^{-1}}\right)}{8.8\ \text{min}} = 7.9 \times 10^{-2}\ \text{min}^{-1}$

13.24 (a) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.15\ \text{s}^{-1}} = 4.6\ \text{s}$

(b) $[N_2O_5]_t = [N_2O_5]_0 e^{-kt} = 0.0567\ \text{mol} \cdot \text{L}^{-1} \times e^{-\left(0.15\,\text{s}^{-1} \times 2.0\ \text{s}\right)}$

(c) $t = \dfrac{\ln\left(\dfrac{[A]_0}{[A]_t}\right)}{k} = \dfrac{\ln\left(\dfrac{[N_2O_5]_0}{[N_2O_5]_t}\right)}{k} = \dfrac{\ln\left(\dfrac{0.0567}{0.0135}\right)}{0.15\ \text{s}^{-1}} = 9.6\ \text{s}$

$\qquad = (9.6\ \text{s})\left(\dfrac{1\ \text{min}}{60\ \text{s}}\right) = 0.16\ \text{min}$

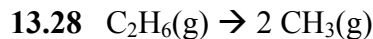**13.26** $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{5.74 \text{ h}^{-1}} = 0.121 \text{ h}$

(a) $\dfrac{[A]}{[A]_0} = \dfrac{1}{8} = \left(\dfrac{1}{2}\right)^3$; therefore, 3 half-lives elapse

$t = 3 \times 0.121 \text{ h} = 0.363 \text{ h}$

(b) $t = \dfrac{\ln\left(\dfrac{1}{0.05}\right)}{5.74 \text{ h}^{-1}} = 0.52 \text{ h}$

(c) $t = \dfrac{\ln\left(\dfrac{[A]_0}{[A]_t}\right)}{k} = \dfrac{\ln 10}{5.74 \text{ h}^{-1}} = 0.40 \text{ h}$

13.28 $C_2H_6(g) \rightarrow 2\ CH_3(g)$

(a) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{1.98 \text{ h}^{-1}} = 0.350 \text{ h}$

(b) $t = \dfrac{\ln\left(\dfrac{[N_2O_5]_0}{[N_2O_5]}\right)}{k} = \dfrac{\ln\left(\dfrac{1.15 \times 10^{-3} \text{ mol/0.5 L}}{2.35 \times 10^{-4} \text{ mol/0.5 L}}\right)}{1.98 \text{ h}^{-1}} = 0.802 \text{ h}$

(c) Because the volume is fixed,

$\ln\left(\dfrac{\text{mass}_0}{\text{mass left}}\right) = kt = \left(\dfrac{1.98}{\text{h}}\right)\left(\dfrac{1 \text{ h}}{60 \text{ min}}\right)(45 \text{ min}) = 1.48$

$\text{mass left} = \dfrac{\text{mass}_0}{e^{1.48}} = \dfrac{6.88 \text{ mg}}{4.39} = 1.57 \text{ mg}$

13.30 $[A]_{95s} = 0.035 \text{ mol} \cdot \text{L}^{-1} - \dfrac{1 \text{ mol A}}{2 \text{ mol B}} \times 0.0120 \text{ (mol B)} \cdot \text{L}^{-1} = 0.0275 \text{ mol} \cdot \text{L}^{-1}$
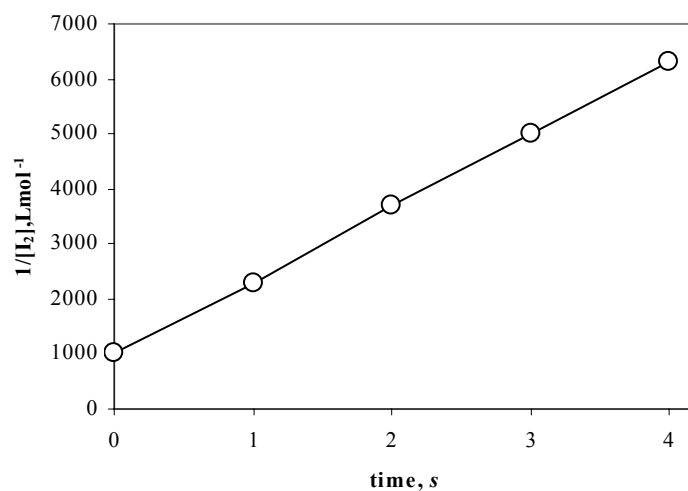
$k = \dfrac{\ln\left(\dfrac{[A]_0}{[A]_t}\right)}{t} = \dfrac{\ln\left(\dfrac{0.0335}{0.0275}\right)}{95 \text{ s}} = 2.1 \times 10^{-3} \text{ s}^{-1}$

$[A]_t = 0.0335 \text{ mol} \cdot \text{L}^{-1} - \dfrac{1 \text{ mol A}}{2 \text{ mol B}} \times 0.0190 \text{ (mol B)} \cdot \text{L}^{-1} = 0.024 \text{ mol} \cdot \text{L}^{-1}$

$t = \dfrac{\ln\left(\dfrac{0.0335}{0.024}\right)}{2.1 \times 10^{-3} \text{ s}^{-1}} = 1.6 \times 10^2 \text{ s}$

additional time $= 160 \text{ s} - 95 \text{ s} = 6 \times 10^1 \text{s}$

13.32 (a)

time, s	$[I_2](mol \cdot L^{-1})$	$1/[I_2](mol \cdot L^{-1})$
0	0.00100	1000
1	0.00043	2300
2	0.00027	3700
3	0.00020	5000
4	0.00016	6300

(b) It can be seen that a plot of $1/[I_2]$ versus time is a straight line with an intercept of 1000 L mol^{-1} and a slope of 1300 L mol^{-1} s^{-1}. Therefore, the reaction is second order with a rate constant $k = 1.3 \cdot 10^{3}$ L mol^{-1} s^{-1}.

13.34 Start by finding an expression for the half-life of a second-order reaction:

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

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

Therefore, $1 + [A]_0 kt_{1/2} = 2$, $kt_{1/2} = 1$, and

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

Also, for a second order reaction,

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

(a) $k = \dfrac{1}{t_{1/2}[A]_0} = \dfrac{1}{(100 \text{ s})(2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})} = 4.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

(b) $[A]_t = \dfrac{[A]_0}{1 + [A]_0 kt}$

$$[A] = \frac{0.30 \text{ mol A}}{\text{L}} - \left(\frac{0.010 \text{ mol C}}{\text{L}}\right)\left(\frac{3 \text{ mol A}}{1 \text{ mol C}}\right) = 0.27 \ (\text{mol A}) \cdot \text{L}^{-1}$$

$$k = \frac{\dfrac{1 \text{ L}}{0.27 \text{ mol}} - \dfrac{1 \text{ L}}{0.30 \text{ mol}}}{200 \text{ s}} = 1.9 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

13.36 Using equations introduced in the previous problem:

(a) $t_{1/2} = \dfrac{1}{k[A]_0} = \dfrac{1}{(0.54 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(0.20 \text{ mol} \cdot \text{L}^{-1})} = 9.3 \text{ s}$

(b) $\frac{1}{16}[A]_0 = (0.0625)(0.20 \text{ mol} \cdot \text{L}^{-1}) = 0.0125 \text{ mol} \cdot \text{L}^{-1} = [A]$

$$t = \frac{\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0}}{k} = \frac{\dfrac{1}{0.0125 \text{ mol} \cdot \text{L}^{-1}} - \dfrac{1 \text{ L}}{0.200 \text{ mol} \cdot \text{L}^{-1}}}{0.54 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 1.4 \times 10^2 \text{ s}$$

(c) $\frac{1}{9}[A]_0 = 0.111... \times 0.20 \text{ mol} \cdot \text{L}^{-1} = 0.022 \text{ mol} \cdot \text{L}^{-1} = [A]$

13.38 $rate = -\dfrac{1}{a}\dfrac{d[A]}{dt} = k[A]^2$

$\dfrac{d[A]}{[A]^2} = -ak \ dt$

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

$\displaystyle\int_{[A]_0}^{[A]_t} \dfrac{d[A]}{[A]^2} = -ak\int_0^t dt$

$[A]_0^{-1} - [A]_t^{-1} = -akt$, and $[A]_t^{-1} = akt + [A]_0^{-1}$

13.40 Given: $\dfrac{d[A]}{dt} = -k[A]^n$, we can derive an expression for the amount

of time needed for the inital 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:

$$\int_{[A]_0}^{[A]_t} [A]^{-n} d[A] = \int_0^t -k dt = -\frac{1}{n-1}\left[[A]_t^{-(n-1)} - [A]_0^{-(n-1)}\right] = -kt$$
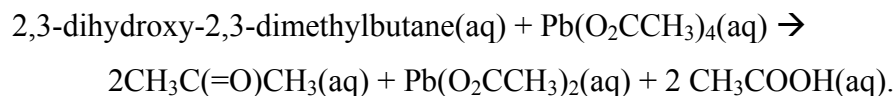
To obtain an expression for the half-life, let $[A]_t = \frac{1}{2}[A]_0$ and $t = t_{1/2}$:

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

solving for the half-life:

$$t_{1/2} = \frac{-\dfrac{[A]_0^{-(n-1)}}{n-1}\left(\tfrac{1}{2}^{-(n-1)} - 1^{-(n-1)}\right)}{k}$$

13.42 The overall reaction is:

2,3-dihydroxy-2,3-dimethylbutane(aq) + $Pb(O_2CCH_3)_4$(aq) $\rightarrow$

$\qquad$ $2CH_3C(=O)CH_3$(aq) + $Pb(O_2CCH_3)_2$(aq) + 2 CH_3COOH(aq).

The intermediate is:
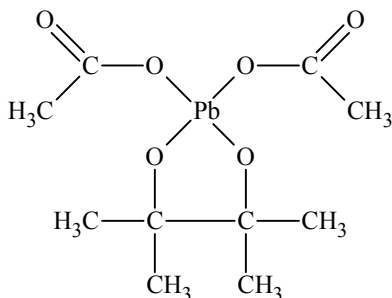
13.44 The second step is rate-determining; therefore,

rate = $k[I^-][HClO]$, but HClO is an intermediate and must be eliminated.

$k_1[ClO^-][H_2O] = k_1'[HClO][OH^-]$

giving

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

Substituting, we write: $\text{rate} = k_2 \left(\frac{k_1}{k_1'}\right) \frac{[\text{ClO}^-][\text{H}_2\text{O}][\text{I}^-]}{[\text{OH}^-]}$
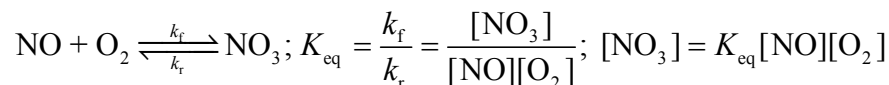
Because H_2O is the solvent, $[\text{H}_2\text{O}] = $ constant; therefore

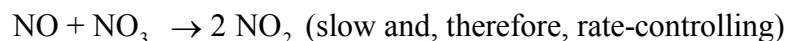$$\text{rate} = k \frac{[\text{ClO}^-][\text{I}^-]}{[\text{OH}^-]}$$

13.46 The rate increases in proportion to the first power of $[\text{O}_2]$ and to the second power of $[\text{NO}]$. Therefore, for $2\,\text{NO}(g) + \text{O}_2(g) \rightarrow 2\,\text{NO}_2(g)$, we can write this rate expression: $\text{rate} = k[\text{NO}]^2[\text{O}_2]$

First, consider mechanism (a):

Step 1:

$$\text{NO} + \text{O}_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{NO}_3; K_{eq} = \frac{k_f}{k_r} = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}; [\text{NO}_3] = K_{eq}[\text{NO}][\text{O}_2]$$

Step 2:

$\text{NO} + \text{NO}_3 \rightarrow 2\,\text{NO}_2$ (slow and, therefore, rate-controlling)

$\text{rate} = k_2[\text{NO}][\text{NO}_3] = k_2 K_{eq}[\text{NO}]^2[\text{O}_2]$, or

$\text{rate} = k[\text{NO}]^2[\text{O}_2]$, with $k = k_2 K_{eq}$, which agrees with

the experimental result.

In mechanism (b), step 1 is rate-controlling and is second order with respect to $[\text{NO}]$, but does not involve $[\text{O}_2]$. Because the other reactions are fast, the expected rate equation would be: $\text{rate} = k[\text{NO}]_2$, but this does not agree with the observed rate law.

13.48 (a) True (b) True (c) True

13.50 The overall rate of formation of A is $\text{rate} = -k[\text{A}]^2 + k'[\text{B}]^2$ because the first reaction reduces [A] while the second increases [A]. Given the 1:1 stoichiometry of the reaction, if no B was present at the beginning of the

reaction, [A] and [B] at any time are related by the equation:

$[A]+[B]=[A]_o$ where $[A]_o$ is the initial concentration of A. Therefore,

$$\frac{d[A]}{dt} = -k[A]^2 + k'([A]_o - [A])^2 = (k+k')[A]^2 + k'\left([A]_0^2 - 2[A]_o[A]\right)$$

The solution of this first-order differential equation is:

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

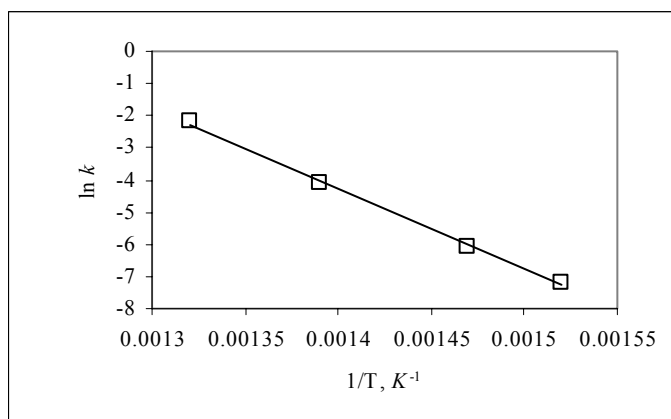As $t \to \infty$ the concentrations reach their equilibrium values given by:

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

taking the ratio of products over reactants we see that:

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

13.52 (a) Prepare the following table and graph:

T, K	1/T, K^{-1}	k, s^{-1}	ln k
660	1.52×10^{-3}	7.2×10^{-4}	−7.2
680	1.47×10^{-3}	2.2×10^{-3}	−6.1
720	1.39×10^{-3}	1.7×10^{-2}	−4.1
760	1.32×10^{-3}	0.11	−2.2

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

The slope of the plot can be determined from a graphing program using a least squares fitting routine or from two points on the graph. The slope from the graphing program held here gave a value for the slope of -2.52×10^4. From two points:

$$\text{slope of plot} = -\frac{E_a}{R} = \frac{[-2.2-(-7.2)]K}{(1.32-1.52)\times10^{-3}} = -2.5 \times 10^4 \text{ K}$$

$E_a = -\text{slope} \times R = 2.5 \times 10^4 \text{ K} \times 8.314 \times 10^{-3} \text{ kJ} \cdot K^{-1} \cdot mol^{-1} = 2.1 \times 10^2$ kJ·mol^{-1}

(b) By inspecting the graph ($T = 400°C = 673$ K; $\frac{1}{T} = 1.49 \times 10^{-3}$), we can adequately estimate

$\ln k = -6.5$, $k = 2 \times 10^{-3}$ s^{-1}

The value of k can also be calculated as follows:

$$\ln\left(\frac{k'}{k}\right) = \frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T'}\right] = 2.5 \times 10^4 \text{ K}\left[\frac{1}{673 \text{ K}} - \frac{1}{760 \text{ K}}\right] = 4.3$$

$\frac{k'}{k} = 70$ (one significant figure), $k = \frac{0.11}{70} = 2 \times 10^{-3}$

13.54 $k' = $ rate constant at $T' = 630$ K

$$E_a = \frac{R \ln\left(\frac{k'}{k}\right)}{\left(\frac{1}{T} - \frac{1}{T'}\right)} = \frac{\left(0.08314 \text{ kJ} \cdot K^{-1} \cdot mol^{-1}\right)\ln\left(\frac{6.0 \times 10^{-5}}{2.4 \times 10^{-6}}\right)}{\left(\frac{1}{575 \text{ K}} - \frac{1}{630 \text{ K}}\right)}$$

$E_a = 1.8 \times 10^2 \text{ kJ} \cdot mol^{-1}$

13.56 $k' = $ rate constant at $T' = 37°C = 3130$ K

$$\ln\left(\frac{k'}{k}\right) = \frac{38 \text{ kJ} \cdot \text{mol}^{-1}}{\left(0.08314 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\right)}\left(\frac{1}{298 \text{ K}} - \frac{1}{310 \text{ K}}\right) - 0.59$$

$$\frac{k'}{k} = 1.8, \ k' = 1.8 \times 1.5 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} = 2.7 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

13.58 $\ln\left(\dfrac{k'}{k}\right) = \dfrac{E_a}{R}\left(\dfrac{1}{T} - \dfrac{1}{T'}\right) = \dfrac{E_a}{R}\left(\dfrac{T - T'}{TT'}\right)$

$$\ln\left(\frac{k'}{k}\right) = \left(\frac{384 \text{ kJ} \cdot \text{mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\right)\left(\frac{1073 \text{ K} - 973 \text{ K}}{973 \text{ K} \times 1073 \text{ K}}\right)$$

$$\ln\left(\frac{k'}{k}\right) = 81$$

$$k' = 81 \times 5.5 \times 10^{-4} \text{ s}^{-1} = 4.5 \times 10^{-2} \text{ s}^{-1}$$

13.60 (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:

$$K = \frac{k'}{k} = \frac{36.4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}}{24.3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}} = 1.50$$

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

(c) Raising the temperature will increase the rate constant of the reaction with the higher activation barrier relatively more than that 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 less than k', and consequently the equilibrium constant K will decrease. This is consistent with Le Chatelier's principle.

13.62 (a) cat = catalyzed, uncat = uncatalyzed

$$E_{a,cat} = \frac{62}{88} E_a = 0.705 \ E_a$$

$$\frac{\text{rate(cat)}}{\text{rate(uncat)}} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{\text{a,cat}}/RT}}{Ae^{-E_{\text{a}}/RT}} = \frac{e^{-0.705\,E_{\text{a}}/RT}}{e^{-E_{\text{a}}/RT}} = e^{0.295\,E_{\text{a}}/RT}$$

$$= e^{0.295 \times 88\ \text{kJ·mol}^{-1}/RT} = e^{\frac{26\ \text{kJ·mol}^{-1}}{RT}} = e^{\frac{26\ \text{kJ·mol}^{-1}}{(8.314\times10^{-3}\ \text{kJ·K}^{-1}\text{·mol}^{-1})(300\ \text{K})}}$$

$$= 3 \times 10^4$$

(b) The last step of the calculation is repeated with $T = 500$ K:

$$\frac{\text{rate (cat)}}{\text{rate (uncat)}} = e^{\frac{26\ \text{kJ·mol}^{-1}}{RT}} = e^{\frac{26\ \text{kJ·mol}^{-1}}{(8.314\times10^{-3}\ \text{kJ·K}^{-1}\text{·mol}^{-1})(500\ \text{K})}} = 5 \times 10^2$$

The rate enhancement is lower at higher temperatures.

13.64 cat = catalyzed, uncat = uncatalyzed

$$\frac{\text{rate (cat)}}{\text{rate (uncat)}} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = 500 = \frac{Ae^{-E_{\text{a,cat}}/RT}}{Ae^{-E_{\text{a}}/RT}}$$

$$\ln 500 = \frac{-E_{\text{a,cat}}}{RT} + \frac{E_{\text{a}}}{RT}$$

$$E_{\text{a,cat}} = E_{\text{a}} - RT \ln 500$$

$$E_{\text{a,cat}} = 106\ \text{kJ·mol}^{-1} - (8.314 \times 10^{-3}\ \text{kJ·K}^{-1}\text{·mol}^{-1})(310\ \text{K})(\ln 500)$$

$$= 90\ \text{kJ·mol}^{-1}$$

13.66 Overall reaction:

$CH_3COOCH_2CH_3(aq) + H_2O(aq) \rightarrow CH_3COOH(aq) \rightarrow CH_3CH_2OH(aq)$
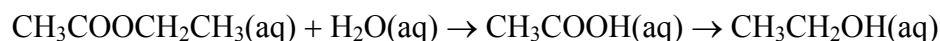
The intermediate is ethoxide ion, $CH_3CH_2O^-$. The catalyst is OH^-.

13.68 (a) True. (b) True. (c) False. The equilibrium constant for a reaction is unaffected by the presence of a catalyst. (d) False. The pathway of a reaction is altered by a catalyst but the beginning and ending points are the same, so the amount of energy released (or gained) is not affected by the presence of a catalyst.

13.70 The Michaelis-Menten mechanism of enzyme reaction:

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + product$$
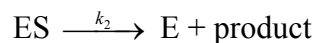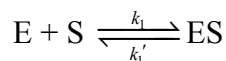
Where E, S, and ES represent the enzyme, substrate, and enzyme-substrate complex, respectively. The Michaelis constant is:

$$K_M = \frac{k_1' + k_2}{k_1}$$

If this constant increases, the rates of the two reactions that lead to decomposition of the enzyme-substrate complex increase compared to the rate of the enzyme-substrate formation reaction. Therefore, a high Michaelis constant indicates an unstable enzyme-substrate complex.

13.72 (a) The best way to determine reaction order is to prepare plots of [A] versus time, ln[A] versus time, and 1/[A] versus time. The first will give a linear relationship when the reaction is zero order with respect to [A], the second will be linear when the reaction is first order with respect to [A], and the last will be linear when the reaction is second order with respect to [A]. These plots are shown below.
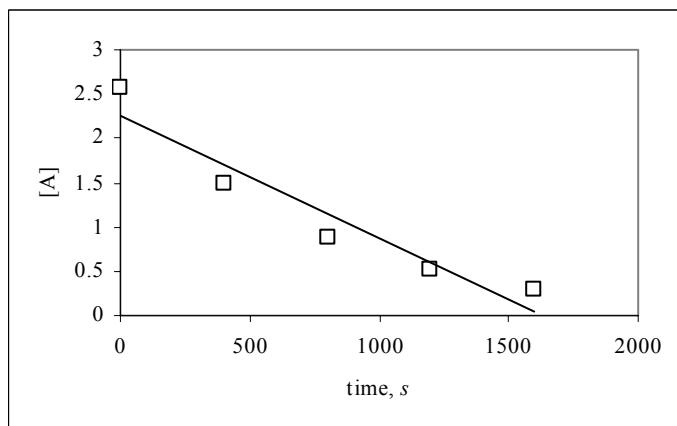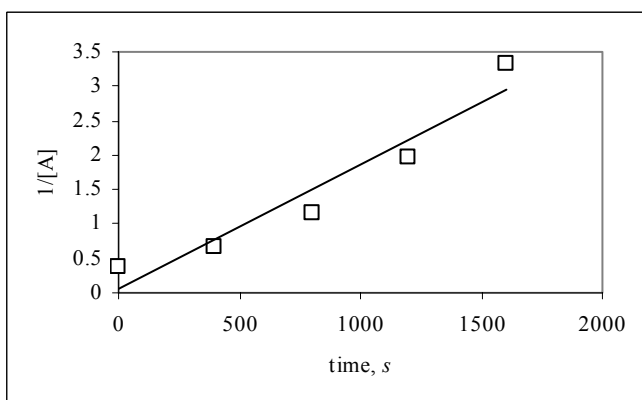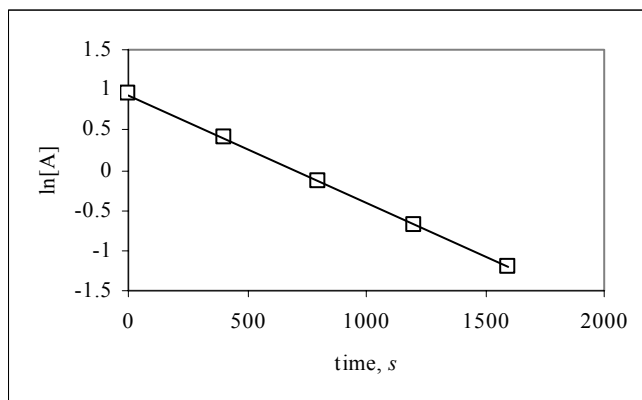
As can be readily seen from the graphs, the only one that gives a straight line relationship is the plot of ln[A] versus time, indicating that the reaction is first order with respect to [A].

(b) The rate constant for the reaction can be determined from the slope of the plot of ln[A] versus time. Because $\ln[A]_t = -kt + \ln[A]_0$, the slope of the line will be $-k$ and the intercept should correspond to $\ln[A]_0$. The equation determined from the graph is $\ln[A] = -0.0013\,\tau + 0.9415$. Therefore, $k = 0.0013\ \text{s}^{-1}$ and $[A]_0$ is calculated to be 2.56, which is in good agreement with the known starting concentration.

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

$[H_2O_2]_t = [H_2O_2]_0 e^{-kt}$

$[H_2O_2]_t = 0.35\ \text{mol·L}^{-1} \times e^{(-0.0410\ \text{min}^{-1} \times 10\ \text{min})}$

$= 0.23\ \text{mol·L}^{-1}$

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(b) $\ln\left(\dfrac{[A]_t}{[A]_0}\right) = kt$

$\ln\left(\dfrac{0.50}{0.10}\right) = 0.0410 \text{ min}^{-1} \times t$

$t = \dfrac{\ln 5}{0.0410 \text{ min}^{-1}} = 39 \text{ min}$

(c) A reduction of $\dfrac{1}{4}$, means $\dfrac{3}{4}$ remains.

$t = \dfrac{\ln\left(\dfrac{[H_2O_2]_0}{[H_2O_2]}\right)}{k} = \dfrac{\ln\left(\dfrac{4}{3}\right)}{0.0410 \text{ min}^{-1}} = 7.0 \text{ min}$
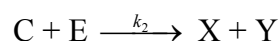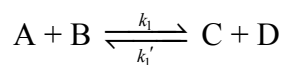
(d) A reduction of 75%, means 25% or $\dfrac{1}{4}$ remains.

$t = \dfrac{\ln\left(\dfrac{[H_2O_2]_0}{[H_2O_2]}\right)}{k} = \dfrac{\ln\left(\dfrac{4}{1}\right)}{k} = \dfrac{1.39}{0.0410 \text{ min}^{-1}} = 34 \text{ min}$

13.76 Refer to Figure 13.25b. For an exothermic reaction, the activation energy for the reverse reaction is greater than that for the forward reaction.

$E_{a,reverse} = E_{a,forward} - \Delta H = 100 \text{ kJ·mol}^{-1} - (-200 \text{ kJ·mol}^{-1}) = 300 \text{ kJ·mol}^{-1}$

13.78 The given mechanism is:

$A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} C + D$

$C + E \xrightarrow{k_2} X + Y$

(a) the rate of formation of $X = k_2[C][E]$

The dependence of this rate on the concentration of the intermediate C can be can be removed by applying the steady-state approximation. Setting the rate of formation of C equal to zero and solving for [C]:

rate of formation of $C = 0 = k_1 [A][B] - k_1'[C][D] - k_1 [C][E]$

$$[C] = \frac{k_1[A][B]}{k_1'[D] + k_2[E]}$$

Substituting this expression for [C] into the rate equation for the appearance of X above:

$$\text{rate of formation of X} = \frac{k_2 k_1[A][B][E]}{k_1'[D] + k_2[E]}$$

(b) In the limit of a large excess of E, the denominator of the expression above simplifies to $k_2[E]$ ($k_2[E]$ being much larger than $k_1'[D]$) and the expression for the rate of formation of X becomes:

$$\text{rate of formation of X} = \frac{k_2 k_1[A][B][E]}{k_2[E]} = k_1[A][B]$$

(c) This expression makes physical sense in that if there is a large excess of E, any small amount of C produced will quickly react to form X and Y and stand little chance of reacting with D to reform the reactants. The overall rate of the mechanism would, therefore, depend only on the rate-limiting step, A + B → C + D, making the rate second order overall.

13.80 The overall reaction is 2 $CH_3C(=O)CH_3 \rightarrow CH_3C(=O)CH_2C(OH)(CH_3)_2$.

The intermediates are
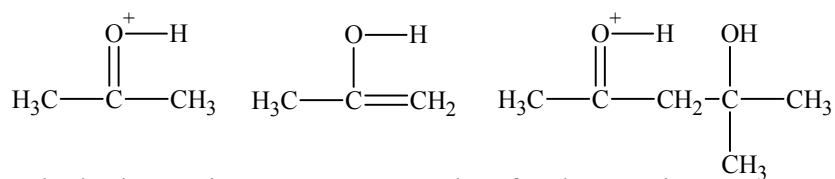
The hydrogen ion serves as a catalyst for the reaction.

13.82 (a)

T, K	$1/T$, K^{-1}	k, 10^{-3} L·mol^{-1}·s^{-1}	$\ln(k \times 10^3)$	$\ln k$
297	0.003 37	4.8	1.57	−5.34
301	0.003 32	7.8	2.05	−4.85
305	0.003 28	13	2.56	−4.34
309	0.003 24	20	3.00	−3.91
313	0.003 19	32	3.47	−3.44
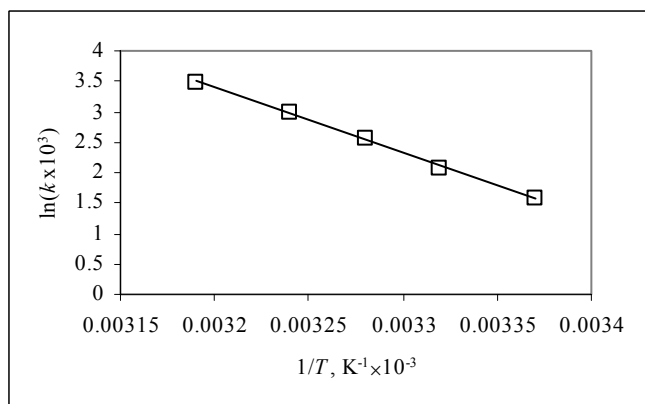
$$\ln k = \ln A - \frac{E_a}{RT}$$

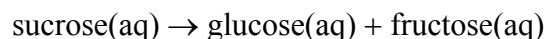slope of straight line above (the ordinates are given as ln k)

$$\text{slope of line} = \frac{(3.47 - 1.57)\ \text{K}}{0.003\ 19\ -0.003\ 37} = -1.1 \times 10^4\ \text{K} = -\frac{E_a}{R}$$

$E_a = (1.1 \times 10^4\ \text{K})(8.314\ 51 \times 10^{-3}\ \text{kJ·K}^{-1}\text{·mol}^{-1}) = 91\ \text{kJ·mol}^{-1}$

(b) $T = 310$ K, $1/T = 3.23 \times 10^{-3}$ K^{-1}

From the plot, $\ln (k \times 10^3) \cong 3.10$, $k \times 10^3 \cong 22$, $k \cong 2.2 \times 10^{-2}$ L·mol^{-1}·s^{-1}

(c) The balanced equation is

sucrose(aq) $\rightarrow$ glucose(aq) + fructose(aq)

We will use the enthalpies of formation for the solid based upon the assumption that the solvation of the sugars is negligible. In fact, this is not unreasonable, because the solvation energy of the sucrose should largely compensate for the solvation of the glucose and fructose in the Hess' Law calculation.
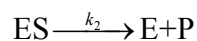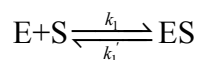
$\Delta H°_{\text{rxn}} = -1268$ kJ·mol^{-1} + -1266 kJ·mol^{-1} − (−2222 kJ·mol^{-1})

$= -312 \text{ kJ·mol}^{-1}$

The overall reaction profile will be
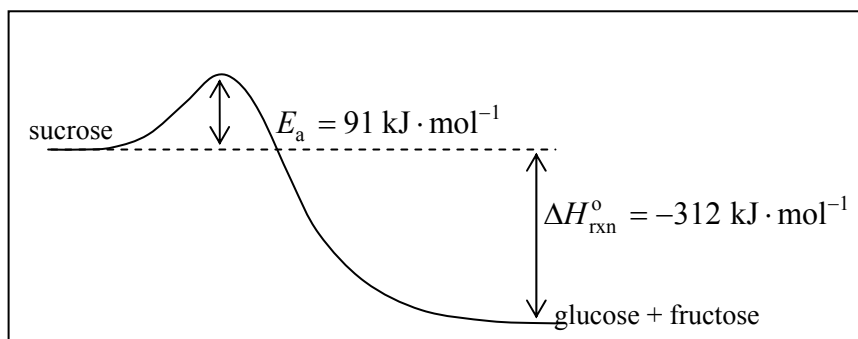
13.84 (a) The mechanism assumed is

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \overset{k_2}{\longrightarrow} E + P$$

Where E is the free enzyme, S is the substrate, ES is the enzyme-substrate complex, and P is the product.

The rate-determining step is the formation of products from the activated complex ES, so we can write

rate = k_2 [ES]

But because ES is an intermediate, we cannot leave it in the final rate expression. We will make a steady-state approximation in order to determine the concentration of ES present in solution. We also need to realize that $[E]_0$ is the starting concentration of enzyme. Because a significant portion of the enzyme will be bound to the substrate, the actual concentration of E at any given time will be equal to $[E]_0 - [ES]$.

In the steady-state approach, the rate of formation of the activated complex ES added to its rate of disappearance will be set equal to 0.

Rate of formation of ES = $k_1[E][S] = k_1([E]_0 - [ES])[S]$

Rate of disappearance of ES = $-k_2$ [ES] $+ -k_1'[ES]$

$k_1([E]_0 - [ES])[S] + (-k_2 [ES] - k_1'[ES]) = 0$

$k_1([E]_0 - [ES])[S] - (k_2 + k_1'[ES]) = 0$

$k_1([E]_0 - [ES])[S] = (k_2 + k_1'[ES])$

$k_1[E]_0[S] - k_1[ES][S] = (k_2 + k_1')[ES]$

$(k_2 + k_1')[ES] + k_1[ES][S] = k_1[E]_0[S]$

$[ES](k_2 + k_1' + k_1[S]) = k_1[E]_0[S]$

$$[ES] = \frac{k_1[E]_0[S]}{k_2 + k_1' + k_1[S]}$$

The rate expression then becomes

$$\text{rate} = k_2[ES] = \frac{k_2 k_1[E]_0[S]}{k_2 + k_1' + k_1[S]}$$

Dividing both numerator and denominator by k_1, we obtain

$$\text{rate} = \frac{k_2[E]_0[S]}{\dfrac{k_2 + k_1'}{k_1} + [S]}$$

$$= \frac{k_2[E]_0[S]}{K_M + [S]}$$

q.e.d.

 [S]

(b) It is easy to confirm that the rate is independent of substrate concentration at high concentrations of substrate by noting that under these conditions $[S] \gg K_M$ so that $K_M + [S] \approx [S]$. The [S] in numerator and denominator will cancel, leaving rate = $k_2[E]_0$.

13.86 According to collision theory, the rate of a reaction is dictated by the frequency of collisions and the fraction of collisions that supply sufficient energy to initiate the reaction. As stated in the "How Do We Do That" box on page 513:

Rate of reaction = (collision frequency) × (fraction with sufficient energy)

The collision frequency is calculated using:

collision frequency = $\sigma v_{rel} N_A^2 [A][B]$

where the relative velocity, v_{rel} is:

$$v_{rel} = \left(\frac{8RT}{\pi\mu}\right)^{1/2}$$

and the fraction of collisions providing at least enough energy to overcome the activation energy for the reaction is given by:

fraction with sufficient energy $= e^{-E_a/RT}$

If we take the reactants to be A and B, the ratio of reaction rates: rate (320 K) / rate (300 K) is:

$$\frac{\text{rate (320 K)}}{\text{rate (300 K)}} = \frac{\sigma\left(v_{rel,\,320\,K}\right) N_A^2 [A][B]}{\sigma\left(v_{rel,\,300\,K}\right) N_A^2 [A][B]} \cdot \frac{e^{-E_a/R \cdot 320\,K}}{e^{-E_a/R \cdot 300\,K}}$$

$$= \frac{\sigma\left(\left(\dfrac{8R \cdot 320\text{ K}}{\pi\mu}\right)^{1/2}\right) N_A^2 [A][B]}{\sigma\left(\left(\dfrac{8R \cdot 300\text{ K}}{\pi\mu}\right)^{1/2}\right) N_A^2 [A][B]} \cdot \frac{e^{-E_a/R \cdot 320\,K}}{e^{-E_a/R \cdot 300\,K}}$$

Canceling those terms which are not dependent on the temperature, this expression simplifies to:

$$\frac{\text{rate (320 K)}}{\text{rate (300 K)}} = \frac{(320\text{ K})^{1/2}}{(300\text{ K})^{1/2}} \cdot \frac{e^{-E_a/R \cdot 320\,K}}{e^{-E_a/R \cdot 300\,K}}$$

$$= 1.033 \cdot e^{\left(-E_a/R \cdot 320\,K\right) + \left(E_a/R \cdot 300\,K\right)}$$

$$= 1.033 \cdot e^{\left(25\text{ kJ·mol}^{-1}/0.0083145\text{ kJ·K}^{-1}\text{·mol}^{-1}\right)\left(\frac{1}{300\text{ K}} - \frac{1}{320\text{ K}}\right)}$$

$$= 1.9$$

13.88 The reaction between A and B has two possible pathways that lead to different products:

$A + B \rightarrow C + D$ (1)

$A + B \rightarrow E + F$ (2)
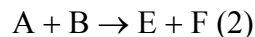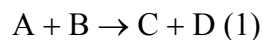
Reaction (1) proceeds by a mechanism in which A first fragments into C and G. Mechanism for reaction (1):

$A \rightarrow C + G$ slow

$B + G \rightarrow D$ fast
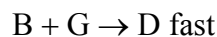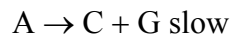
Reaction (2) proceeds by a direct combination of A and B having a second-order, bimolecular rate law.

(a) Reaction (1) will have a rate law dependent only upon the concentration of A, rate = $k_1[A]$, whereas reaction (2) will have a rate law that depends upon both A and B, rate = $k_2[A][B]$. If we wish the rate of reaction (2) to proceed faster, then we can increase the concentration of [B]. This should not affect the rate of reaction (1).

(b) The rate at which A disappears will be determined by summing the rates of consumption of A for both pathways: $-\dfrac{d[A]}{t} = k_1[A] + k_2[A][B]$.

(c) We can use the equation from (b) to determine the rate constants because we know the rates at two sets of concentrations. The rate of disappearance of A for Experiment 1 is going to be 0.0045 mol·L^{-1}·h^{-1} + 0.0015 mol·L^{-1}·h^{-1} (because 1 mole of A is consumed for each mole of C produced and for each mole of E produced). For Experiment 2, the value is 0.0045 mol·L^{-1}·h^{-1} + 0.000 50 mol·L^{-1}·h^{-1}. This data allows us to construct two simultaneous equations:

0.0060 mol·L^{-1}·h^{-1} = k_1(0.100 mol·L^{-1})
$\qquad\qquad\qquad + k_2$(0.100 mol·L^{-1})(0.100 mol·L^{-1})

0.0050 mol·L^{-1}·h^{-1} = k_1(0.100 mol·L^{-1})
$\qquad\qquad\qquad + k_2$(0.100 mol·L^{-1})(0.050 mol·L^{-1})

or

0.0060 mol·L^{-1}·h^{-1} = k_1(0.100 mol·L^{-1}) + k_2(0.0100 mol^2·L^{-2})

0.0050 mol·L^{-1}·h^{-1} = k_1(0.100 mol·L^{-1}) + k_2(0.0050 mol^2·L^{-2})

Solving these simultaneously, we obtain

$k_2 = 0.020$ L·mol^{-1}·h^{-1} and $k_1 = 0.040$ h^{-1}

13.90 Let P = pollutant

(a) rate = R − $k[P]_{eq}$ = 0 at equilibrium

$[P]_{eq} = + \left(\dfrac{R}{k} \right)$

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(b) Because $[P]_{eq}$ = constant, there is no overall half-life, but on average, for an individual molecule, there is a 50% probability that it will have decayed after $t_{1/2}$ where

$$t_{1/2} = \frac{0.693}{k}$$

13.92 (a) $K = \dfrac{k_1}{k_1'}$ (1)

(b) From Section 13.7

$$\ln\frac{k_1}{k_2} = -\frac{E_{a(forward)}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2)$$

$$\ln\frac{k_1'}{k_2'} = -\frac{E_{a(reverse)}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

(c) and (d) To show the relationship between the kinetic and thermodynamic treatment, we need to find an expression for K in terms of the rate constants. This can be done by subtracting equation (3) from equation (2):

$$\ln\frac{k_1}{k_2} - \ln\frac{k_1'}{k_2'} = -\frac{E_{a(forward)}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) - \left[-\frac{E_{a(reverse)}}{r}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\ln\left(\frac{k_1}{k_2} \cdot \frac{k_2'}{k_1'}\right) = -\left(\frac{E_{a(forward)}}{R} - \frac{E_{a(reverse)}}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{K_1}{K_2} = -\frac{(E_{a(forward)} - E_{a(reverse)})}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This is now in a form similar to the van't Hoff equation derived in Chapter 9:

$$\ln\frac{K_1}{K_2} = -\frac{\Delta H^\circ_r}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

in which ΔH°_r corresponds to $E_{a(forward)} - E_{a(reverse)}$.

13.94 (a) Table 13.1 gives the rate constant for the reaction. Using the data from Appendix 2A, the equilibrium constant for the reaction cyclopropane → propene can be calculated at 773 K. From that value and the value for the rate of conversion of cyclopropane to propene, the rate constant for the conversion of propene to cyclopropane can be estimated:

$\Delta H°_r = 20.42$ kJ·mol^{-1} − 53.30 kJ·mol^{-1} = −32.88 kJ·mol^{-1}

$\Delta S°_r = 266.6$ J·K^{-1}·mol^{-1} − 237.4 J·K^{-1}·mol^{-1} = 29.2 J·K^{-1}·mol^{-1}

$\Delta G°_r = -32.88$ kJ·mol^{-1} − (773 K)(29.2 J·K^{-1}·mol^{-1})/(1000 J·kJ^{-1})

$\qquad = -55.5$ kJ·mol^{-1}

$\Delta G°_r = -RT \ln K$

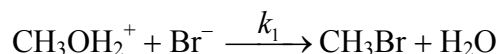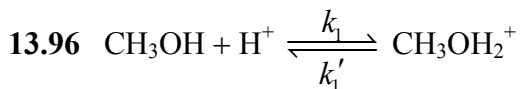$(-55.5$ kJ·mol$^{-1})(1000$ J·kJ$^1) = (8.314$ J·K^1·mol$^1)(773$ K) $\ln K$

$\ln K = 8.64$

$K = 5.7 \times 10^3$

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

$5.7 \times 10^3 = \dfrac{6.7 \times 10^{-4}\ \text{s}^{-1}}{k'}$

$k' = 1.2 \times 10^{-7}\ \text{s}^{-1}$

(b) The reaction is exothermic, which means that the activation energy for the reverse reaction will be larger than the activation energy for the forward reaction. This means that the rate constant for the conversion of propene to cyclopropane will be decreased more than the rate constant of the conversion of cyclopropane to propene upon decreasing the temperature. The result is that K will become larger as T is lowered.

13.96 $CH_3OH + H^+ \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} CH_3OH_2{}^+$

$CH_3OH_2{}^+ + Br^- \xrightarrow{k_1} CH_3Br + H_2O$

(a) The rate law will be based upon the second step, which is the slow step of the reaction.

rate $= k_2[CH_3OH_2^+][Br^-]$

The rate law cannot be left in this form because $CH_3OH_2^+$ is a reactive

intermediate. We can express the concentration of $CH_3OH_2^+$ in terms of

the reactants and products, using the fast equilibrium established in the

first step.

$$K = \frac{k_1}{k_1'} = \frac{[CH_3OH_2^+]}{[CH_3OH][H^+]}$$

$$[CH_3OH_2^+] = \frac{k_1}{k_1'}[CH_3OH][H^+]$$

The rate then becomes

$$rate = \frac{k_2 k_1}{k_1'}[CH_3OH][H^+][Br^-]$$

The steady state approximation is similar to the fast equilibrium approach,

except that k_2 may not be very much smaller than k_1'. This means that the

rate of the reaction to final products is fast enough to disturb the

equilibrium established in the pre-equilibrium step. To use this

approximation, we set the rate of formation of the intermediate equal to its

rate of disappearance:

rate of formation of $CH_3OH_2^+ = k_1[CH_3OH][H^+]$

rate of disappearance of $CH_3OH_2^+ = k_1'[CH_3OH_2^+] + k_2[CH_3OH_2^+][Br^-]$

$k_1'[CH_3OH_2^+] + k_2[CH_3OH_2^+][Br^-] = k_1[CH_3OH][H^+]$

$[CH_3OH_2^+](k_1' + k_2[Br^-]) = k_1[CH_3OH][H^+]$

$$[CH_3OH_2^+] = \frac{k_1[CH_3OH][H^+]}{k_1' + k_2[Br^-]}$$

We then place this expression in the same rate law as in part (a).

$$rate = \frac{k_2 k_1[CH_3OH][H^+][Br^-]}{k_1' + k_2[Br^-]}$$

(b) When k_2 is very much less than k_1', the expressions will be the same.

They will also be the same at low concentrations of Br^-.

(c) At high concentrations of Br^-, the steady-state approximation rate will have $k_2[Br^-] \gg k_1'$. Under those conditions, the rate law becomes rate $= k_1[CH_3OH][H^+]$. The fast equilibrium rate law would not change at high concentrations of Br^-.

13.98 The reaction profile as given:
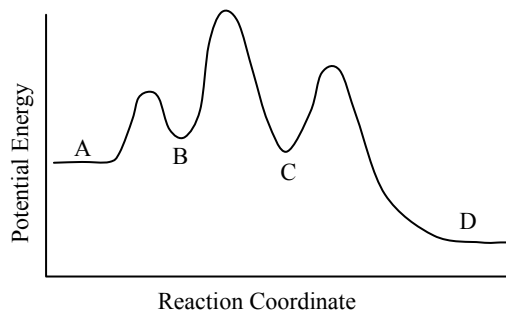
(a) Overall, the reaction is exothermic. The product possesses less potential energy than the reactant. (b) There are two intermediates, B and C. (c) There are three activated complexes, one complex at the maximum in the curve between the reactant A and the intermediate B, an activated complex between the intermediates B and C, and a third activated complex between the intermediate C and the final product D. (d) The reaction to form C from B would be rate limiting as this step has the largest activation barrier. (e) The reaction to form D from C would be the fastest as the energy released on going from the activated complex between the intermediates B and C to the intermediate C is sufficient to send C over the final reaction barrier to D.

13.100 (a) To convert from one isomer to the other, a single C-C bond is broken and a single C-N bond is formed, giving an approximate enthalpy of reaction of:

$305 \text{ kJ} \cdot \text{mol}^{-1} - 348 \text{ kJ} \cdot \text{mol}^{-1} = -43 \text{ kJ} \cdot \text{mol}^{-1}$. (b) The rate constant at 300 K is found using:

$\ln\frac{k'}{k} = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$. Substituting into this equation we find:

$\ln\frac{k'}{6.6\times10^{-4}\ \text{s}^{-1}} = \frac{161000\ \text{J}\cdot\text{mol}^{-1}}{8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\left(\frac{1}{500\ \text{K}} - \frac{1}{300\ \text{K}}\right)$

Solving for k':

$k' = 4.04\times10^{-15}\ \text{s}^{-1}$

At this rate, the time required to reduce the initial concentration of the isomer by 75% is found by:

$\ln\frac{[CH_3NC]_t}{[CH_3NC]_0} = \ln(0.75) = -k\cdot t = -4.04\times10^{-15}\ \text{s}^{-1}\cdot t$

$t = 7.12\times10^{13}\ \text{s}$

(c) We begin by finding the rate constant at which the concentration of the isomer will reduce by 75% in one hour:

$\ln\frac{[CH_3NC]_t}{[CH_3NC]_0} = \ln(0.75) = -k\cdot t = -k\cdot 1\ \text{h}\left(\frac{60\ \text{min}}{\text{h}}\right)\left(\frac{60\ \text{s}}{\text{min}}\right)$

Solving for k:

$k = 7.99\times10^{-5}\ \text{s}^{-1}$

We can now determine at what temperature this rate constant is reached using the equation from part (b) above:

$\ln\frac{k'}{k} = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$.

$\ln\frac{7.99\times10^{-5}\ \text{s}^{-1}}{6.6\times10^{-4}\ \text{s}^{-1}} = \frac{161000\ \text{J}\cdot\text{mol}^{-1}}{8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\left(\frac{1}{500\ \text{K}} - \frac{1}{T}\right)$

Solving for T:

$T = 474\ \text{K}$

(d) Argon serves as a collision partner. Collisions between the CH₃NC (g) and argon atoms provide the energy needed to overcome the activation energy and allow the isomerization reaction to proceed toward products. The argon atoms also serve as an energy sink, accepting the energy released during the isomerization reaction. (e) At high argon concentrations, collisions resulting in reaction are between the CH₃NC (g) and argon atoms:

CH₃NC (g) + Ar (g) → CH₃CN (g) +Ar (g).
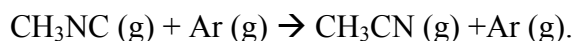
Given this elementary reaction one would predict that the reaction was first order with respect to CH_3NC (g) concentration and would appear first order overall if the concentration of Ar (g) was large and unchanging. If, however, the concentration of Ar (g) was greatly reduced, the isomerization reaction would also proceed through collisions between CH_3NC (g) molecules, making the reaction second order with respect to CH_3NC (g).