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

1.3 mol MnO_4^- L^{-1} min-1

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

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

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

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

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

13.18 (a) and (b) rate = $k[\mathrm{NO_2}]_o[\mathrm{O_3}]_o$, 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.

$$k = \frac{\text{rate}}{[\mathrm{NO_2}]_o[\mathrm{O_3}]_o}$$

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

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

42.9

(d) $$\text{rate} = \left(\frac{\overset{42.9}{\cancel{4.3\times 10^{-7}}}\ \mathrm{L}}{\mathrm{mmol\cdot s}}\right)\left(\frac{0.66\times\cancel{10^{-3}}\ \mathrm{mmol}}{\mathrm{L}}\right)\left(\frac{0.18\times\cancel{10^{-3}}\ \mathrm{mmol}}{\mathrm{L}}\right)$$

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

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

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

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

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

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

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

$$k = \frac{\ln\left(\dfrac{0.040\text{ mol}\cdot\mathrm{L}^{-1}}{0.020\text{ mol}\cdot\mathrm{L}^{-1}}\right)}{8.8\text{ min}} = 7.9\times10^{-2}\text{ min}^{-1}$$

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

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.

13.64 cat = catalyzed, uncat = uncatalyzed

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

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

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

$$E_{\text{a,cat}} = 106\text{ kJ}\cdot\text{mol}^{-1} - (8.314\times10^{-3}\text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(310\text{ K})(\ln 500)$$

$$= 90\text{ kJ}\cdot\text{mol}^{-1}$$

13.78 The given mechanism is:

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

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

(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]

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

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

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

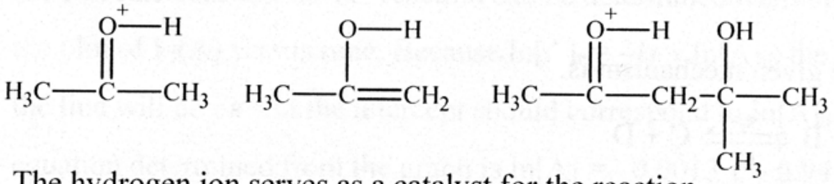
(b) In the limit of a large excess of E, the denominator of the expression above simplifies to k_2[E] (k_2[E] being much larger than k_1'[D]) and the expression for the rate of formation of X becomes:

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

(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.

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

$CH_3OH_2^+ + Br^- \xrightarrow{k_{\cancel{1}2}} CH_3Br + H_2O$

(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

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

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).

$$\text{rate} = \frac{k_2 k_1[\text{CH}_3\text{OH}][\text{H}^+][\text{Br}^-]}{k_1' + k_2[\text{Br}^-]}$$

(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 $k_2[\text{Br}^-] >> k_1'$. Under those conditions, the rate law becomes rate = $k_1[\text{CH}_3\text{OH}][\text{H}^+]$. The fast equilibrium rate law would not change at high concentrations of Br^-.