Section 6.5: Rate Law
Tutorial 1 Practice, page 380
1. (a) The order of reaction with respect to A is 2. When the initial concentration of A is doubled, the rate increases by a factor of 4, or 2^2, so, the exponent of the concentration of reactant A is 2. The order of reaction with respect to B is 1. When the initial concentration of B is doubled, the rate is doubled, or multiplied by 2^1, so the exponent of the concentration of reactant B is 1. The order of reaction with respect to B is 0. When the initial concentration of C is doubled, there is no effect on rate; this is equivalent to multiplying by 2^0, so the exponent of the concentration of reactant C is 0.

(b) The rate law equation for the reaction is $k[A]^2[B]$.

2. (a) Given: $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$; $[CO(g)]_{initial} = 0.025$ mol/L;

$[NO_2(g)]_{initial} = 0.055$ mol/L; $rate_{initial} = 2.5$ mol/(L×s); orders of reaction

Required: initial rate if $[CO(g)]_{initial}$ is doubled

Solution: The rate law for the reaction is

rate $= k[CO(g)][NO_2(g)]$

Since the rate is first order with respect to carbon monoxide, if the initial concentration of carbon monoxide is doubled, the initial rate will be multiplied by 2^1, or 2.
The new rate is
$2 \times (2.5$ mol/(L·s)$) = 5.0$ mol/(L·s)

Statement: If the initial concentration of carbon monoxide is doubled, the initial rate of reaction will be 5.0 mol/L·s.

(b) Given: rate $= [CO(g)][NO_2(g)]$; $rate_{initial} = 2.5$ mol/(L×s)

Required: initial rate if $[NO_2(g)]_{initial}$ is tripled

Solution: Since the rate is first order with respect to carbon monoxide, if the initial concentration of nitrogen dioxide is tripled, the initial rate will be multiplied by 3^1, or 3.
The new rate is
$3 \times (2.5$ mol/(L·s)$) = 7.5$ mol/(L·s)

Statement: If the initial concentration of nitrogen dioxide is doubled, the initial rate of reaction will be 7.5 mol/(L·s).

(c) The reaction is first order with respect to carbon monoxide, so doubling the $CO(g)$ concentration will double the reaction rate. The reaction is first order with respect to nitrogen dioxide, so tripling the $NO_2(g)$ concentration will triple the new reaction rate:
$2 \times 3 \times (2.5$ mol/(L·s)$) = 15$ mol/(L·s)

3. (a) Given: $2 NO(g) + Cl_2(g) \rightarrow 2 NOCl(g)$; experimental data provided in Table 3
Required: the rate law equation

Analysis: rate $= k[NO(g)]^m[Cl_2(g)]^n$

To determine the orders of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for m and n into the rate equation along with 1 set of data from the table.

Solution: Step 1. Find m.

Look at the data from runs 2 and 3, because the initial concentration of nitric oxide changed while the concentration of chlorine remained constant. When the initial concentration of nitric oxide doubled, the rate of reaction was multiplied by 4, or 2^2. The exponent m in the rate law equation is therefore 2, and the order of reaction with respect to NO(g) is 2.

Step 2. Find n.

Look at the data from runs 1 and 2, because the initial concentration of chlorine changed while the concentration of nitric oxide remained constant. When the initial concentration of chlorine doubled, the rate of reaction doubled. The exponent n in the rate law equation is therefore 1, and the order of reaction with respect to Cl_2(g) is 1.

Step 3. Therefore, for this reaction,

$$\text{rate} = k[NO(g)]^2[Cl_2(g)]$$

Statement: The rate law equation is rate = $k[NO(g)]^2[Cl_2(g)]$.

(b) Given: rate = $k[NO(g)]^2[Cl_2(g)]$; $[NO(g)]_{initial}$ = 0.10 mol/L;

$[Cl_2(g)]_{initial}$ = 0.10 mol/L; $\text{rate}_{initial}$ = 1.8 mol/(L×s)

Required: the rate constant, k

Analysis: To find k, rearrange the rate law equation to solve for k and enter the values provided.

$$\text{rate} = k[NO(g)]^2[Cl_2(g)]$$

$$k = \frac{\text{rate}}{[NO(g)]^2[Cl_2(g)]}$$

Solution:
$$k = \frac{\text{rate}}{[NO(g)]^2[Cl_2(g)]}$$

$$= \frac{0.18 \text{ mol/(L×s)}}{(0.10 \text{ mol/L})^2(0.10 \text{ mol/L})}$$

$$k = 1.8 \times 10^2 \text{ L}^2/(\text{mol}^2 \times s)$$

Statement: The rate constant, k, is $1.8 \times 10^2 \text{ L}^2/(\text{mol}^2 \times s)$.

4. (a) Given: $2 I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2 SO_4^{2-}(aq)$; experimental data provided in Table 4

Required: the rate law equation

Analysis: rate = $k[I^-(aq)]^m[S_2O_8^{2-}(aq)]^n$

Solution: Step 1. Find m.

Look at the data from runs 2 and 1, because the initial concentration of I^-(aq) changed while the concentration of $S_2O_8^{2-}$(aq) remained constant. When the initial concentration of I^-(aq) doubled, the rate of reaction was multiplied by 2, or 2^1. The exponent m in the rate law equation is therefore 1, and the order of reaction with respect to I^-(aq) is 1.

Step 2. Find n.

Look at the data from runs 3 and 1, because the initial concentration of $S_2O_8^{2-}$(aq) changed while the concentration of I^-(aq) remained constant. When the initial concentration of $S_2O_8^{2-}$(aq) doubled, the rate of reaction doubled. The exponent n in the rate law equation is therefore 1, and the order of reaction with respect to $S_2O_8^{2-}$(aq) is 1.

Step 3. Therefore, for this reaction,

$$\text{rate} = k[I^-(aq)][S_2O_8^{2-}(aq)]$$

Statement: The rate law equation is $r = k[I^-(aq)][S_2O_8^{2-}(aq)]$.

(b) Given: experimental data provided in Table 4

Required: the rate constant, k, and an average value for the initial rate constant

Analysis: $\text{rate} = k[I^-(aq)][S_2O_8^{2-}(aq)]$

$$k = \frac{\text{rate}}{[I^-(aq)][S_2O_8^{2-}(aq)]}$$

Calculate the rate constant for each run of the investigation and then average the values.

Solution: Run 1: $k = \dfrac{\text{rate}}{[I^-(aq)][S_2O_8^{2-}(aq)]}$

$$= \frac{12.5 \times 10^{-6}\ \text{mol/(L}\times\text{s)}}{(0.080\ \text{mol/L})(0.040\ \text{mol/L})}$$

$$k = 3.9 \times 10^{-3}\ \text{L/(mol}\times\text{s)}$$

Run 2: $k = \dfrac{\text{rate}}{[I^-(aq)][S_2O_8^{2-}(aq)]}$

$$= \frac{6.25 \times 10^{-6}\ \text{mol/(L}\times\text{s)}}{(0.040\ \text{mol/L})(0.040\ \text{mol/L})}$$

$$k = 3.9 \times 10^{-3}\ \text{L/(mol}\times\text{s)}$$

Run 3: $k = \dfrac{\text{rate}}{[I^-(aq)][S_2O_8^{2-}(aq)]}$

$$= \frac{6.25 \times 10^{-6}\ \text{mol/(L}\times\text{s)}}{(0.080\ \text{mol/L})(0.020\ \text{mol/L})}$$

$$k = 3.9 \times 10^{-3}\ \text{L/(mol}\times\text{s)}$$

Run 4: $k = \dfrac{\text{rate}}{[I^-(aq)][S_2O_8^{2-}(aq)]}$

$$= \frac{5.00 \times 10^{-6}\ \text{mol/(L}\times\text{s)}}{(0.032\ \text{mol/L})(0.040\ \text{mol/L})}$$

$$k = 3.9 \times 10^{-3}\ \text{L/(mol}\times\text{s)}$$

Run 5: $k = \dfrac{\text{rate}}{[\text{I}^-(aq)][\text{S}_2\text{O}_8^{2-}(aq)]}$

$= \dfrac{7.00 \times 10^{-6} \text{ mol/(L}\times\text{s)}}{(0.060 \text{ mol/L})(0.030 \text{ mol/L})}$

$k = 3.9 \times 10^{-3} \text{ L/(mol}\times\text{s)}$

Statement: The value for the rate constant, k, for each investigation is 3.9×10^{-3} L/(mol×s).

5. (a) Given: 2 A + B + 2 C → 3 D; experimental data provided in Table 5
Required: order of reaction with respect to each of the reactants
Analysis: To determine the orders of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for m and n into the rate equation along with 1 set of data from the table.
Solution: Step 1. Find m.
Look at the data from runs 1 and 2, because the initial concentration of A changed while the concentrations of B and C remained constant. When the initial concentration of A doubled, the rate of reaction was multiplied by 4, or 2^2. The exponent m in the rate law equation is therefore 2, and the order of reaction with respect to A is 2.
Step 2. Find n.
Look at the data from runs 1 and 3, because the initial concentration of B changed while the concentrations of A and C remained constant. When the initial concentration of B tripled, the rate of reaction stayed the same. The exponent n in the rate law equation is therefore 0, and the order of reaction with respect to B is 0.
Step 3. Find p.
Look at the data from runs 1 and 4, because the initial concentration of C changed while the concentrations of A and B remained constant. When the initial concentration of C doubled, the rate of reaction doubled. The exponent n in the rate law equation is therefore 1, and the order of reaction with respect to B is 1.
Statement: The reaction is second order with respect to A, zero order with respect to B, and first order with respect to C.
(b) Given: orders of reactions: A = 2, B = 0, C = 1
Required: the rate law equation
Analysis: rate = $k[\text{A}]^m[\text{B}]^n[\text{C}]^p$
Solution: rate = $k[\text{A}]^2[\text{C}]$

Statement: The rate law equation is rate = $k[\text{A}]^2[\text{C}]$.
(c) Given: experimental data provided in Table 4
Required: the rate constant, k
Analysis: rate = $k[\text{A}]^2[\text{C}]$

$k = \dfrac{\text{rate}}{[\text{A}]^2[\text{C}]}$

Calculate the rate constant for each run of the investigation and then average the values.

Solution: Run 1: $k = \dfrac{\text{rate}}{[A]^2[C]}$

$$= \dfrac{3.0 \times 10^{-4} \text{ mol/(L}\times\text{s)}}{(0.10 \text{ mol/L})^2(0.10 \text{ mol/L})}$$

$$k = 0.30 \text{ L}^2/(\text{mol}^2 \times \text{s})$$

Run 2: $k = \dfrac{\text{rate}}{[A]^2[C]}$

$$= \dfrac{1.2 \times 10^{-3} \text{ mol/(L}\times\text{s)}}{(0.20 \text{ mol/L})^2(0.10 \text{ mol/L})}$$

$$k = 0.30 \text{ L}^2/(\text{mol}^2 \times \text{s})$$

Run 3: Same as run 1

Run 4: $k = \dfrac{\text{rate}}{[A]^2[C]}$

$$= \dfrac{6.0 \times 10^{-4} \text{ mol/(L}\times\text{s)}}{(0.10 \text{ mol/L})^2(0.20 \text{ mol/L})}$$

$$k = 0.30 \text{ L}^2/(\text{mol}^2 \times \text{s})$$

Statement: The rate constant, k, for the reaction is $0.30 \text{ L}^2/(\text{mol}^2 \times \text{s})$.

(d) Given: $[A] = [B] = [C] = 0.40$ mol/L; rate $= k[A]^2[C]$; $k = 0.30 \text{ L}^2/(\text{mol}^2 \times \text{s})$
Required: the rate of production of D
Solution: rate $= k[A]^2[C]$

$$= (0.30 \text{ L}^2/(\text{mol}^2 \cdot \text{s}))(0.40 \text{ mol/L})^2(0.40 \text{ mol/L})$$

$$\text{rate} = 1.9 \times 10^{-2} \text{ mol/(L}\cdot\text{s)}$$

Statement: The rate of production of D is $1.9 \times 10^{-2} \text{ mol/(L}\times\text{s)}$.

Section 6.5 Questions, page 382
1. Given: $2 \text{ N}_2\text{O}_5(g) \rightarrow 4 \text{ NO}_2(g) + \text{O}_2(g)$; experimental data provided in Table 7
Required: the rate law equation, and the rate constant, k
Analysis: There is only one reactant, so the rate law is
rate $= k[\text{N}_2\text{O}_5(g)]^x$

Solution: Compare the ratio of change in $[N_2O_5(g)]$ and change in initial rate:

$$\frac{[N_2O_5(g)]_{\text{initial Run 2}}}{[N_2O_5(g)]_{\text{initial Run 1}}} = \frac{0.190 \text{ mol/L}}{0.0750 \text{ mol/L}} = 2.53$$

$$\frac{\text{initial rate}_{\text{Run 2}}}{\text{initial rate}_{\text{Run 1}}} = \frac{2.26 \times 10^{-3} \text{ mol/(L}\times\text{s)}}{8.90 \times 10^{-4} \text{ mol/(L}\times\text{s)}} = 2.53$$

The change in rate is directly proportional to the change in concentration, so $x = 1$.

rate $= k[N_2O_5(g)]$

$$k = \frac{\text{rate}}{[N_2O_5(g)]}$$

$$= \frac{8.90 \times 10^{-4} \text{ mol/(L}\times\text{s)}}{0.0750 \text{ mol/L}}$$

$$k = 1.19 \times 10^{-2} \text{ s}^{-1}$$

Statement: The rate law for the equation is rate $= k[N_2O_5(g)]$, and the rate constant, k, is

$1.19 \times 10^{-2} \text{ s}^{-1}$.

2. (a) Given: $2 \text{ NOCl(g)} \rightarrow 2 \text{ NO(g)} + \text{Cl}_2(g)$; experimental data provided in Table 8
Required: the rate law equation

Analysis: rate $= k[\text{NOCl(g)}]^m$

Solution: When the initial concentration doubled, the rate of reaction was multiplied by 4, or 2^2. When the initial concentration tripled, the rate of reaction was multiplied by 9, or 3^2. When the initial concentration was quadrupled, the rate of reaction was multiplied by 16, or 4^2. The exponent m in the rate law equation is therefore 2, and the order of reaction with respect to nitrosyl chloride gas is 2. Therefore, for this reaction,

rate $= k[\text{NOCl(g)}]^2$

Statement: The rate law equation is rate $= k[\text{NOCl(g)}]^2$.

(b) Given: rate $= k[\text{NOCl(g)}]^2$
Required: the rate constant, k
Analysis: To find k, rearrange the rate law equation to solve for k and enter the values provided.

rate $= k[\text{NOCl(g)}]^2$

$$k = \frac{\text{rate}}{[\text{NOCl(g)}]^2}$$

Solution: $k = \dfrac{\text{rate}}{[\text{NOCl(g)}]^2}$

$$= \frac{5.98 \times 10^4 \text{ mol/(L}\times\text{s)}}{(3.0 \times 10^{-1} \text{mol/L})^2}$$

$$= \frac{5.98 \times 10^4 \text{ mol}/(\cancel{L}\times\text{s})}{(3.0 \times 10^{-1})^2 \text{ mol}^{\cancel{2}}/\text{L}^{\cancel{2}}}$$

$$k = 6.6 \times 10^5 \text{ L/(mol}\times\text{s)}$$

Statement: The rate constant, k, is 6.6×10^5 L/(mol×s).

3. (a) Given: $I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$; experimental data provided in Table 9

Required: the rate law equation

Analysis: rate $= k\,[I^-(aq)]^m[OCl^-(aq)]^n$

Solution: Step 1. Find m.

Look at the data from runs 1 and 2, because the initial concentration of $I^-(aq)$ changed while the concentration of $OCl^-(aq)$ remained constant. When the initial concentration of $I^-(aq)$ doubled, the rate of reaction was multiplied by 2, or 2^1. The exponent m in the rate law equation is therefore 1, and the order of reaction with respect to $I^-(aq)$ is 1.

Step 2. Find n.

Look at the data from runs 3 and 4, because the initial concentration of $OCl^-(aq)$ changed while the concentration of $I^-(aq)$ remained constant. When the initial concentration of $OCl^-(aq)$ was multiplied by 8, the rate of reaction was multiplied by 8. The exponent n in the rate law equation and the order of reaction with respect to $OCl^-(aq)$ is 1.

Step 3. Therefore, for this reaction,

rate $= k\,[I^-(aq)][OCl^-(aq)]$

Statement: The rate law equation is rate $= k\,[I^-(aq)][OCl^-(aq)]$.

(b) Given: rate $= k\,[I^-(aq)][OCl^-(aq)]$

Required: the rate constant, k

Analysis: To find k, rearrange the rate law equation to solve for k and enter the values provided.

rate $= k[I^-(aq)][OCl^-(aq)]$

$$k = \frac{\text{rate}}{[I^-(aq)][OCl^-(aq)]}$$

Solution: $k = \dfrac{\text{rate}}{[I^-(aq)][OCl^-(aq)]}$

$$= \frac{7.91\times10^{-2}\ \text{mol/(L}\cdot\text{s)}}{(0.12\ \text{mol/L})(0.18\ \text{mol/L})}$$

$$k = 3.66\,\text{L/(mol}\cdot\text{s)} \text{ (one extra digit carried)}$$

Statement: The rate constant, k, is 3.7 L/(mol×s).

(c) Given: rate $= k[I^-(aq)][OCl^-(aq)]$; $k = 3.66$ L/(mol×s);
$[I^-(aq)] = [OCl^-(aq)] = 0.15$ mol/L

Required: initial rate

Solution: rate $= k[I^-(aq)][OCl^-(aq)]$

$$= (3.66\ \text{L/(mol×s)})(0.15\ \text{mol/L})(0.15\ \text{mol/L})$$

$$\text{rate} = 8.2 \times 10^{-2}\ \text{mol/(L×s)}$$

Statement: The initial rate is 8.2×10^{-2} mol/(L×s).

4. (a) Given rate $= k[Cl_2(g)][NO(g)]^2$, the orders of reaction are $Cl_2(g) = 1$ and $NO(g) = 2$.

(b) If the initial concentration of $Cl_2(g)$ were tripled, the rate would triple because the reaction is first order with respect to $Cl_2(g)$.

(c) If the initial concentration of $NO(g)$ were doubled, the rate would increase fourfold (quadruple) because the reaction is second order with respect to $NO(g)$.

(d) Given: rate $= 0.0242$ mol/L·s; $[Cl_2(g)]_{initial} = [NO(g)]_{initial} = 0.20$ mol/L

Required: the rate constant, k

Analysis: To find k, rearrange the rate law equation to solve for k and enter the values provided.

$$\text{rate} = k[Cl_2(g)][NO(g)]^2$$

$$k = \frac{\text{rate}}{[Cl_2(g)][NO(g)]^2}$$

Solution:
$$k = \frac{\text{rate}}{[Cl_2(g)][NO(g)]^2}$$

$$= \frac{0.0242 \text{ mol/(L·s)}}{(0.20 \text{ mol/L})(0.20 \text{ mol/L})^2}$$

$$k = 3.0 \text{ L}^2/(\text{mol}^2 \cdot s)$$

Statement: The rate constant, k, is $3.0 \text{ L}^2/(\text{mol}^2 \times s)$.

(e) Given: $\text{rate} = k[Cl_2(g)][NO(g)]^2$; $k = 3.0 \text{ L}^2/(\text{mol}^2 \times s)$; $[Cl_2(g)]_{\text{initial}} = 0.44$ mol/L; $[NO(g)]_{\text{initial}} = 0.025$ mol/L

Required: reaction rate

Solution:
$$\text{rate} = k[Cl_2(g)][NO(g)]^2$$

$$= (3.0 \text{ L}^2/(\text{mol}^2 \cdot s))(0.44 \text{ mol/L})(0.025 \text{ mol/L})^2$$

$$= (3.0 \text{ L}^2/(\text{mol}^2 \cdot s))(0.44 \text{ mol/L})[(6.25 \times 10^{-4}) \text{mol}^2/\text{L}^2]$$

$$\text{rate} = 8.2 \times 10^{-4} \text{ mol/(L·s)}$$

Statement: The initial rate is 8.2×10^{-4} mol/(L×s).