Hw - CH14 Prob 1

14 Chemical Kinetics

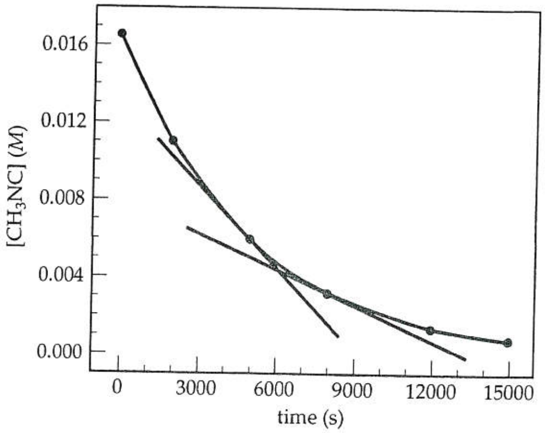
Solutions to Exercises

14.21 (a) *Analyze/Plan*. Follow the logic in Sample Exercises 14.1 and 14.2. *Solve.*

Time (sec)	Time Interval (sec)	Concentration (*M*)	ΔM	Rate (*M*/s)
0		0.0165		
2,000	2,000	0.0110	−0.0055	28×10^{-7}
5,000	3,000	0.00591	−0.0051	17×10^{-7}
8,000	3,000	0.00314	−0.00277	9.23×10^{-7}
12,000	4,000	0.00137	−0.00177	4.43×10^{-7}
15,000	3,000	0.00074	−0.00063	2.1×10^{-7}

(b) $$\frac{\Delta M_B}{\Delta t} = \frac{(0.0165 - 0.00074)\ M}{(15{,}000 - 0)\ s} = 1.0507 \times 10^{-6} = 1.05 \times 10^{-6}\ M/s$$

(c) From the slopes of the lines in the figure at right, the rates are: at 5000 s, $12 \times 10^{-7}\ M/s$; at 8000 s, $5.8 \times 10^{-7}\ M/s$

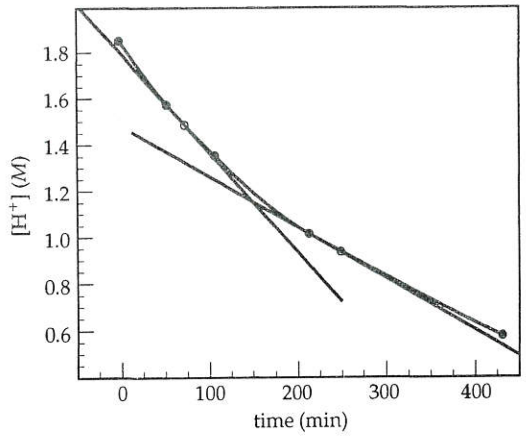


14.22 (a)

Time (min)	Time Interval (min)	Concentration (*M*)	ΔM	Rate (*M*/s)
0.0		1.85		
54.0	54.0	1.58	−0.27	8.3×10^{-5}
107.0	53.0	1.36	−0.22	6.9×10^{-5}
215.0	108	1.02	−0.34	5.2×10^{-5}
430.0	215	0.580	−0.44	3.4×10^{-5}

(b) $$\frac{\Delta M_B}{\Delta t} = \frac{(1.85 - 0.580)\ M}{(430 - 0)\ \text{min}} \times \frac{1\ \text{min}}{60\ s} = 4.9225 \times 10^{-5} = 4.92 \times 10^{-5}\ M/s$$

(c) From the slopes of the lines in the figure at the right, the rates are: at 75.0 min, 4.2×10^{-3} M/min, or 7.0×10^{-5} M/s; at 250 min, 2.1×10^{-3} M/min or 3.5×10^{-5} M/s



14.23 *Analyze/Plan.* Follow the logic in Sample Exercise 14.3. *Solve.*

(a) $-\Delta[H_2O_2]/\Delta t = \Delta[H_2]/\Delta t = \Delta[O_2]/\Delta t$

(b) $-\Delta[N_2O]/2\Delta t = \Delta[N_2]/2\Delta t = \Delta[O_2]/\Delta t$

$-\Delta[N_2O]/\Delta t = \Delta[N_2]/\Delta t = 2\Delta[O_2]/\Delta t$

(c) $-\Delta[N_2]/\Delta t = \Delta[NH_3]/2\Delta t$; $-\Delta[H_2]/3\Delta t = \Delta[NH_3]/2\Delta t$

$-2\Delta[N_2]/\Delta t = \Delta[NH_3]/\Delta t$; $-\Delta[H_2]/\Delta t = 3\Delta[NH_3]/2\Delta t$

(d) $-\Delta[C_2H_5NH_2]/\Delta t = \Delta[C_2H_4]/\Delta t = \Delta[NH_3]/\Delta t$

14.24 (a) rate $= -\Delta[H_2O]/2\Delta t = \Delta[H_2]/2\Delta t = \Delta[O_2]/\Delta t$

(b) rate $= -\Delta[SO_2]/2\Delta t = -\Delta[O_2]/\Delta t = \Delta[SO_3]/2\Delta t$

(c) rate $= -\Delta[NO]/2\Delta t = -\Delta[H_2]/2\Delta t = \Delta[N_2]/\Delta t = \Delta[H_2O]/2\Delta t$

(d) rate $= -\Delta[N_2]/\Delta t = -\Delta[H_2]/2\Delta t = \Delta[N_2H_4]/\Delta t$

14.25 *Analyze/Plan.* Use Equation [14.4] to relate the rate of disappearance of reactants to the rate of appearance of products. Use this relationship to calculate desired quantities. *Solve.*

(a) $\Delta[H_2O]/2\Delta t = -\Delta[H_2]/2\Delta t = -\Delta[O_2]/\Delta t$

H_2 is burning, $-\Delta[H_2]/\Delta t = 0.48$ mol/s

O_2 is consumed, $-\Delta[O_2]/\Delta t = -\Delta[H_2]/2\Delta t = 0.48$ mol/s/2 $= 0.24$ mol/s

H_2O is produced, $+\Delta[H_2O]/\Delta t = -\Delta[H_2]/\Delta t = 0.48$ mol/s

(b) The change in total pressure is the sum of the changes of each partial pressure. NO and Cl_2 are disappearing and NOCl is appearing.

$-\Delta P_{NO}/\Delta t = -56$ torr/min

$-\Delta P_{Cl_2}/\Delta t = \Delta P_{NO}/2\Delta t = -28$ torr/min

$+\Delta P_{NOCl}/\Delta t = -\Delta P_{NO}/\Delta t = +56$ torr/min

$\Delta P_T/\Delta t = -56$ torr/min $- 28$ torr/min $+ 56$ torr/min $= -28$ torr/min

14.26 (a) $-\Delta[C_2H_4]/\Delta t = \Delta[CO_2]/2\Delta t = \Delta[H_2O]/2\Delta t$

$-2\Delta[C_2H_4]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[H_2O]/\Delta t$

C_2H_4 is burning, $-\Delta[C_2H_4]/\Delta t = 0.036\ M/s$

CO_2 and H_2O are produced, at twice the rate that C_2H_4 is consumed.

$\Delta[CO_2]/\Delta t = \Delta[H_2O]/\Delta t = 2(0.036)\ M/s = 0.072\ M/s$

(b) In this reaction, pressure is a measure of concentration.

$-\Delta[N_2H_4]/\Delta t = -\Delta[H_2]/\Delta t = \Delta[NH_3]/2\Delta t$

N_2H_4 is consumed, $-\Delta[N_2H_4]/\Delta t = 74$ torr/hr

H_2 is consumed, $-\Delta[H_2]/\Delta t = 74$ torr/hr

NH_3 is produced at twice the rate that N_2H_4 and H_2 are consumed,

$\Delta[NH_3]/\Delta t = -2\Delta[N_2H_4]/\Delta t = 2(74)$ torr/hr $= 148$ torr/hr

$\Delta P_T/\Delta t = (+148$ torr/hr $- 74$ torr/hr $- 74$ torr/hr$) = 0$ torr/hr

Rate Laws (section 14.3 and 14.2)

14.27 *Analyze/Plan.* Follow the logic in Sample Exercises 14.4 and 14.5. *Solve.*

(a) If [A] is doubled, there will be no change in the rate or the rate constant. The overall rate is unchanged because [A] does not appear in the rate law; the rate constant changes only with a change in temperature.

(b) The reaction is zero order in A, second order in B and second order overall.

(c) Units of $k = \dfrac{M/s}{M^2} = M^{-1}\ s^{-1}$

14.28 (a) rate = $k[A][C]^2$

(b) rate is proportional to [A], rate doubles

(c) rate is not affected by [B], no change

(d) rate changes as $[C]^2$, rate increases by a factor of 3^2 or 9

(e) rate increases by a factor of $(3)(3)^2 = 27$

(f) rate decreases by a factor of $(1/2)(1/2)^2 = 1/8$

14.29 *Analyze/Plan.* Follow the logic in Sample Exercise 14.4. *Solve.*

(a) rate = $k[N_2O_5] = 4.82 \times 10^{-3}\ s^{-1}\ [N_2O_5]$

(b) rate = $4.82 \times 10^{-3}\ s^{-1}\ (0.0240\ M) = 1.16 \times 10^{-4}\ M/s$

(c) rate = $4.82 \times 10^{-3}\ s^{-1}\ (0.0480\ M) = 2.31 \times 10^{-4}\ M/s$

When the concentration of N_2O_5 doubles, the rate of the reaction doubles.

(d) rate = $4.82 \times 10^{-3}\ s^{-1}\ (0.0120\ M) = 5.78 \times 10^{-5}\ M/s$

When the concentration of N_2O_5 is halved, the rate of the reaction is halved.

14.30 (a) rate = $k[H_2][NO]^2$

(b) rate = $(6.0 \times 10^4\ M^{-2}\ s^{-1})(0.035\ M)^2(0.015\ M) = 1.1\ M/s$

(c) rate = $(6.0 \times 10^4\ M^{-2}\ s^{-1})\ (0.10\ M)^2\ (0.010\ M) = 6.0\ M/s$

(d) rate = $(6.0 \times 10^4\ M^{-2}\ s^{-1})\ (0.010\ M)^2\ (0.030\ M) = 0.18\ M/s$

14.31 *Analyze/Plan.* Write the rate law and rearrange to solve for k. Use the given data to calculate k, including units. *Solve.*

(a, b) rate = $k[CH_3Br][OH^-]$; $k = \dfrac{\text{rate}}{[CH_3Br][OH^-]}$

$$\text{at 298 K, } k = \frac{0.0432\ M/s}{(5.0 \times 10^{-3}\ M)(0.050\ M)} = 1.7 \times 10^2\ M^{-1}s^{-1}$$

(c) Since the rate law is first order in $[OH^-]$, if $[OH^-]$ is tripled, the rate triples.

(d) If $[OH^-]$ and $[CH_3Br]$ both triple, the rate increases by a factor of (3)(3) = 9.

14.32 (a, b) rate = $k[C_2H_5Br][OH^-]$; $k = \dfrac{\text{rate}}{[C_2H_5Br][OH^-]}$

$$\text{at 298 K, } k = \frac{1.7 \times 10^{-7}\ M/s}{[0.0477\ M][0.100\ M]} = 3.6 \times 10^{-5}\ M^{-1}s^{-1}$$

(c) Adding an equal volume of ethyl alcohol reduces both $[C_2H_5Br]$ and $[OH^-]$ by a factor of two. new rate = (1/2)(1/2) = 1/4 of old rate

14.33 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6. *Solve.*

(a) From the data given, when $[OCl^-]$ doubles, rate doubles. When $[I^-]$ doubles, rate doubles. The reaction is first order in both $[OCl^-]$ and $[I^-]$. rate = $k[OCl^-][I^-]$

(b) Using the first set of data:

$$k = \frac{\text{rate}}{[OCl^-][I^-]} = \frac{1.36 \times 10^{-4}\ M/s}{(1.5 \times 10^{-3}\ M)(1.5 \times 10^{-3}\ M)} = 60.444 = 60\ M^{-1}\ s^{-1}$$

(c) $$\text{rate} = \frac{60.444}{M\text{-}s}(2.0 \times 10^{-3}\ M)(5.0 \times 10^{-4}\ M) = 6.0444 \times 10^{-5} = 6.0 \times 10^{-5}\ M/s$$

14.34 (a) From the data given, when $[ClO_2]$ increases by a factor of 3 (experiment 2 to experiment 1), the rate increases by a factor of 9. When $[OH^-]$ increases by a factor of 3 (experiment 2 to experiment 3), the rate increases by a factor of 3. The reaction is second order in $[ClO_2]$ and first order in $[OH^-]$. rate = $k[ClO_2]^2[OH^-]$.

(b) Using data from Expt 2:

$$k = \frac{\text{rate}}{[ClO_2]^2\,[OH^-]} = \frac{0.00276\ M/s}{(0.020\ M)^2\ (0.030\ M)} = 2.3 \times 10^2\ M^{-2}s^{-1}$$

(c) rate = $2.3 \times 10^2\ M^{-2}\ s^{-1}\ (0.100\ M)^2(0.050\ M) = 0.115 = 0.12\ M/s$

14.35 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

(a) Doubling [NH_3] while holding [BF_3] constant doubles the rate (experiments 1 and 2). Doubling [BF_3] while holding [NH_3] constant doubles the rate (experiments 4 and 5).

Thus, the reaction is first order in both BF_3 and NH_3; rate = k[BF_3][NH_3].

(b) The reaction is second order overall.

(c) From experiment 1: $k = \dfrac{0.2130\ M/s}{(0.250\ M)(0.250\ M)} = 3.41\ M^{-1}\ s^{-1}$

(Any of the five sets of initial concentrations and rates could be used to calculate the rate constant k. The average of these 5 values is $k_{avg} = 3.408 = 3.41\ M^{-1}s^{-1}$)

(d) rate = $3.408\ M^{-1}s^{-1}(0.100\ M)(0.500\ M) = 0.1704 = 0.170\ M/s$

14.36 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

(a) Doubling [NO] while holding [O_2] constant increases the rate by a factor of 4 (experiments 1 and 2). Doubling [O_2] while holding [NO] constant doubles the rate (experiments 2 and 3). The reaction is second order in [NO] and first order in [O_2]. rate = $k[NO]^2[O_2]$

(b, c) From experiment 1: $k_1 = \dfrac{1.41 \times 10^{-2}\ M/s}{(0.0126\ M)^2\ (0.0125\ M)} = 7105 = 7.11 \times 10^3\ M^{-2}s^{-1}$

$k_2 = 0.113/(0.0252)^2(0.0250) = 7118 = 7.12 \times 10^3\ M^{-2}\ s^{-1}$

$k_3 = 5.64 \times 10^{-2}/(0.0252)^2(0.125) = 7105 = 7.11 \times 10^3\ M^{-2}\ s^{-1}$

$k_{avg} = (7105 + 7118 + 7105)/3 = 7109 = 7.11 \times 10^3\ M^{-2}\ s^{-1}$

(d) rate = $7.109 \times 10^3\ M^{-2}s^{-1}\ (0.0750\ M)^2(0.0100\ M) = 0.3999 = 0.400\ M/s$

(e) The data are given in terms of the disappearance of NO. Use Equation [14.4] to relate the disappearance of NO to the disappearance of O_2.

$-\Delta[NO]/2\Delta t = -[O_2]/\Delta t$

For the concentrations given in part (d), $\Delta[NO]/\Delta t = 0.400\ M/s$.

$\Delta[O_2]/\Delta t = \Delta[NO]/2\Delta t = 0.400\ M/s/2 = 0.200\ M/s$

14.37 *Analyze/Plan.* Follow the logic in Sample Exercise 4.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

(a) Increasing [NO] by a factor of 2.5 while holding [Br_2] constant (experiments 1 and 2) increases the rate by a factor 6.25 or $(2.5)^2$. Increasing [Br_2] by a factor of 2.5 while holding [NO] constant increases the rate by a factor of 2.5. The rate law for the appearance of NOBr is: rate = $\Delta[NOBr]/\Delta t = k[NO]^2[Br_2]$.

(b) From experiment 1: $k_1 = \dfrac{24\ M/s}{(0.10\ M)^2\ (0.20\ M)} = 1.20 \times 10^4 = 1.2 \times 10^4\ M^{-2}\ s^{-1}$