CHM 112.009
Additional Problems – Chapter 14

1. For the reaction

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}\ O_2$$

the initial concentration of H_2O_2 is 0.1108 M and 12 s later the concentration is 0.1060 M. What is the initial rate of this reaction expressed in M/sec and M/min?

2. In the reaction

$$2\ A + 2\ B \longrightarrow C + 2\ D$$

the rate of disappearance of A is -2.2×10^{-4} M·s^{-1}. What is the:

   (a) rate of disappearance of B?

   (b) rate of formation of C?

   (c) the general rate of reaction?

3. What would be the units of k for a reaction

$$A \longrightarrow \text{Products}$$

for which the order of the reaction was $\frac{1}{2}$?

4. For the reaction

$$2\ A + B \longrightarrow C$$

the rate law is RATE = k[A][B]. Which of the following statements is true – and why?

   (a) The value of k is independent of the initial concentrations $[A]_0$ and $[B]_0$.

   (b) The unit of the rate constant, k, can be determined to be either s^{-1} or min^{-1}.

5. The following rate data was collected for the reaction

$$2\ HgCl_2 + C_2O_4^{2-} \longrightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$$

Experiment	Initial $[HgCl_2]$ mol·L^{-1}	Initial $[C_2O_4^{2-}]$ mol·L^{-1}	Initial Rate mol·L^{-1}·s^{-1}
1	0.105	0.15	1.8×10^{-5}
2	0.105	0.30	7.1×10^{-5}
3	0.052	0.30	3.5×10^{-5}
4	0.052	0.15	8.9×10^{-6}

   (a) Determine the **overall** order of the reaction

   (b) Determine the value of the rate constant k

   (c) What would be the initial rate of the reaction if $[HgCl_2]_0$ = 0.094 M and $[C_2O_4^{2-}]_0$ = 0.19 M?

   (d) Are all four experiments needed to answer questions (a) – (c)?

6. In a reaction

$$A \longrightarrow \text{Products}$$

the following data were obtained. What is the order of the reaction?

Experiment 1: $[A]_0$ = 1.512 M, $[A]_{30sec}$ = 1.496 M

Experiment 2: $[A]_0$ = 2.584 M, $[A]_{60sec}$ = 2.552 M

7. A first order reaction

$$\text{A} \longrightarrow \text{Products}$$

has a rate of reaction of 0.00250 $\text{M}\cdot\text{s}^{-1}$ when [A] = 0.484 M.

   (a) What is the rate constant k for this reaction?

   (b) Do $t_{\frac{3}{4}}$ and $t_{\frac{4}{5}}$ depend on the initial concentration?

8. In the first order decomposition of dinitrogen pentoxide at 335 K

$$\text{N}_2\text{O}_5 \longrightarrow 2\ \text{NO}_2 + \tfrac{1}{2}\ \text{O}_2$$

if one starts with a 2.50 g sample of N_2O_5 at 335 K and, after 109 seconds only 1.50 g remains:

   (a) What is the value of the rate constant?

   (b) What is $t_{\frac{1}{2}}$

   (c) What mass of N_2O_5 will remain after 5.0 minutes?

9. The decomposition of di-tert-butyl peroxide (DTBP) is a first order reaction with a half life of 320 minutes at 135 °C and 100 minutes at 135 °C. Calculate the activation energy, E_a, for this reaction.

10. A reaction has a first order rate constant of 4.82×10^{-5} s^{-1} at 25 °C and 1.41×10^{-2} at 70 °C. Calculate the value of the rate constant at 90 °C.

11. For the reaction

$$\text{A} \longrightarrow 2\ \text{B} + \text{C}$$

the following data are obtained for [A] as a function of time:

$t = 0$ min, [A] = 0.80 M
$t = 8$ min, [A] = 0.60 M
$t = 24$ min, [A] = 0.35 M
$t = 40$ min, [A] = 0.20 M

   (a) Establish the order of the reaction

   (b) What is the value of the rate constant, k

   (c) Calculate the rate of formation of B at 22 min

12. A reaction that is second order in reactant A has $[\text{A}]_0 = 0.200$ M. The half life is 45.6 sec. What is [A] after 3.00 min.

13. Explain why, for the following reaction

$$\text{NO}_2\ (g) + \text{CO}\ (g) \longrightarrow \text{NO}\ (g) + \text{CO}_2\ (g)$$

the mechanism shown below is inconsistent with the measured rate law of $\text{RATE} = k[\text{NO}_2]^2$.

$$2\ \text{NO}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{O}_4 \qquad \text{(fast, equilibrium)}$$

$$\text{N}_2\text{O}_4 + 2\ \text{CO} \xrightarrow{k_2} 2\ \text{NO} + 2\ \text{CO}_2 \qquad \text{(slow)}$$

14. Given that the proposed mechanism is consistent with the rate law $\text{RATE} = k[\text{H}_2][\text{NO}]^2$ for the reaction

$$2\ \text{H}_2\ (g) + 2\ \text{NO}\ (g) \longrightarrow 2\ \text{N}_2\ (g) + 2\ \text{H}_2\text{O}\ (g)$$

PROPOSED MECHANISM:

$$2\ \text{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{O}_2$$

$$\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$$

$$\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}$$

Which step **must** be the rate determining step?