Chem 6
Homework Assignment 1 -- Kinetics 1

Zumdahl 5th ed. Ch. 15, exercises 11-17 (odd), 21, 25, 27, 31, 33, 43-47 (odd)
Zumdahl 5th ed. Ch. 21, exercises 15, 17

1. Consider the hydrolysis of acetyl chloride (CH_3COCl) to produce acetic acid (CH_3COOH) and hydrochloric acid (HCl). Note: water is the solvent.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

Experimentally the rate law is found to be

$$-\,d[CH_3COCl]/dt = k\,[CH_3COCl]\,[H_2O]$$

At the beginning of the reaction, the concentration of CH_3COCl is 0.10 M.

(i) At the beginning of the reaction, what is the concentration of H_2O?
(ii) If the reaction proceeds to completion what is the <u>final</u> concentration of H_2O?
(iii) If $k = 1.16 \times 10^{-3}\ M^{-1}\ s^{-1}$, how long will it take for the concentration of CH_3COCl to be reduced to 0.05 M?

2. The gas phase reaction of nitric oxide, NO, with chlorine, Cl_2, occurs according to the equation:

$$2\,NO + Cl_2 \rightarrow 2\,NOCl$$

The experimental rate law is:

$$(1/2)\,d[NOCl]/dt = k\,[NO]^2\,[Cl_2]$$

A possible reaction mechanism is:

(i) $2\,NO \rightarrow N_2O_2$ (fast, at equilibrium)
(ii) $N_2O_2 + Cl_2 \rightarrow 2\,NOCl$ (slow)

Identify the rate determining step (rds), show that this mechanism is consistent with the rate law, and express the experimental rate constant, k_{exp}, in terms of the rate constants for the elementary processes.

3. An alternative mechanism for the reaction considered in Problem #2 is:

(i) $NO + Cl_2 \rightarrow NO{\bullet}Cl_2$ (fast, at equilibrium)
(ii) $NO{\bullet}Cl_2 + NO \rightarrow 2NOCl$ (slow)

Identify the rds, derive an expression for the rate of production of nitrosyl chloride, NOCl, and hence express the experimental rate constant, k'_{exp}, in terms of the rate constants for the elementary processes. Could kinetic data alone distinguish between the mechanism proposed in this problem and that proposed in Problem #2?

4. The mechanism for the decomposition $2\ NO_2Cl \rightarrow 2\ NO_2 + Cl_2$ is:

(i) $NO_2Cl \rightarrow NO_2 + Cl$
(ii) $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$

If step (i) is at equilibrium and fast relative to step (ii), show that the rate of disappearance of NO_2Cl is given by:
$-\,d[NO_2Cl]/dt = 2\,k_2\,K\,[NO_2Cl]^2\,[NO_2]^{-1}$

5. The rate law of the reaction

$2\ NO(g) + H_2(g) \text{---> } N_2O(g) + H_2O(g)$

is investigated at a certain temperature under pseudo-first-order conditions. The following two experiments are performed:

(1) 2.0 mol/L of NO is mixed with 0.010 mol/L of H_2, and the time dependence of $[H_2]$ is determined, with the following results:

time(s)	$[H_2]$ (M)
0	1.0×10^{-2}
10	6.2×10^{-3}
20	3.8×10^{-3}
30	2.4×10^{-3}

(2) 2.0 mol/L of H_2 is mixed with 0.010 mol/L of NO, and the time dependence of [NO] is determined, with the following results:

time(s)	[NO] (M)
0	1.0×10^{-2}
1000	8.1×10^{-3}
2000	6.8×10^{-3}
3000	5.8×10^{-3}

Determine the rate law of the reaction and the value of the rate constant.