Gazi University Faculty of Engineering
Department of Chemical Engineering
ChE 244 Physical Chemistry, Problem Set #4

PROBLEM SET 4
(Mechanism of Chemical Reactions)

1. The mechanism for the decomposition of N_2O_5 is

$$N_2O_5 + M \underset{k_2}{\overset{k_1}{\leftrightarrow}} NO_2 + NO_3 + M \qquad \text{(slow)}$$

$$NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2 \qquad \text{(slow)}$$

$$NO + NO_3 \xrightarrow{k_4} 2\,NO_2 \qquad \text{(slow)}$$

and the overall reaction is $2N_2O_5 \rightarrow 4NO_2 + O_2$. Find the rate expression.

2. The decomposition of ozone in the gas phase $2O_3 \rightarrow 3O_2$ takes place through the following mechanism

$$O_3 + M \leftrightarrow O_2 + O + M \qquad \text{(slow)}$$

$$O + O_3 \rightarrow 2O_2 \qquad \text{(slow)}$$

Derive the rate law.

3. Derive the rate expression for the reaction $CO + Cl_2 \leftrightarrow COCl_2$ if the mechanism of the reaction is as follows:

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2Cl^* \qquad \text{(fast)}$$

$$Cl^* + CO \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} COCl^* \qquad \text{(fast)}$$

$$COCl^* + Cl_2 \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} COCl_2 + Cl^* \qquad \text{(slow)}$$

4. For the reaction

$$2NO + 2\,H_2 \longrightarrow N_2 + 2H_2O$$

The rate expression for this reaction is given to be third order.

$r_{N2} = k\,[\,NO\,]^2[\,H_2\,]$.

Show that the mechanism given below is consistent with this rate equation.

$$2NO + H_2 \longrightarrow N_2 + 2H_2O_2 \qquad \text{(slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \qquad \text{(fast)}$$

5. Consider the following mechanism:

$$A + B \underset{k_2}{\overset{k_1}{\leftrightarrow}} C$$

$$C \xrightarrow{k_3} D$$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 << k_2$, express the pre-exponential factor A and E_a for the apparent second order rate constant in terms A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

6. The reaction $NO_2Cl = NO_2 + \frac{1}{2} Cl_2$ is first order and appears to follow the mechanism

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

(a) Assuming a steady state for the chlorine atom concentration, show that the emprical first order rate constant can be identified with $2k_1$

(b) The following data were obtained at 180 ^{0}C. In a single experiment the reaction is first order, and the empirical rate constant is represented by k. Show that the reaction is second order at these low gas pressures and calculate the second order rate constant.

c/ 10^{-8}mol cm^{-3}	5	10	15	20
k/ 10^{-4} s^{-1}	1,7	3,4	5,2	6,9

7. The mechanism of the pyrolysis of acetaldehyde at 520 °C and 0.2 bar is

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CO + CH_3$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

What is the rate law for the reaction of acetaldehyde, using the usual assumptions? (As a simplification further reactions of the radical CHO have been omitted and is the rate equation may be ignored.)

8. The equations for $[A_2]$ and $[A_3]$ in section 18.4 give an indeterminate result if $k_1 = k_2$. Rederive the equations, giving $[A_2]$ and $[A_3]$ as functions of time fort he special case that

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_1} A_3$$

9. A dimerization $2A \longrightarrow A_2$ is found to be first order with a half life of 666 s. This somewhat surprising result is explained by postulating the following mechanism

$$A \xrightarrow{k_1} A^* \qquad A^* + A \xrightarrow{k_2} A_2$$

Where $k_2 >> k_1$ (a) What is the value for the rate constant k_1? (b) if the initial concentration of A is 0.05 M, how much time is required to reach [A] =0.0125 M?

10. Consider two consecutive first order nuclear decay reactions with the rate constants k_1 and k_2

$$A \xrightarrow{k_3} B \qquad \text{and} \qquad B \xrightarrow{k_2} C$$

If $k_1 = k_2 = 0.1340$ year^{-1} , draw $[B]/[A]_0$ plot.

11. For the reaction

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

The overall rate expression is third order.

$R_{N2} = k[NO]^2[H_2]$

Show that two mechanism below consistent with rate equation

a)
$$2NO + H_2 \xrightarrow{k_1} N_2 + 2H_2O_2 \quad (slow)$$

$$H_2O_2 + H_2 \xrightarrow{k_2} 2H_2O \qquad (fast)$$

b) $$2NO \underset{k_2}{\overset{k_{\bar{1}}}{\leftrightarrow}} N_2O_2 \text{ (fast)}$$

$$N_2O_2 + H_2 \xrightarrow{k_3} N_2 + 2H_2O \quad slow$$

$$H_2O_2 + H_2 \xrightarrow{k_4} 2H_2O \qquad (fast)$$