Homework 11

1. The following initial-rate data were obtained on the rate of binding of glucose with the enzyme hexokinase present at a concentration of 1.34 mmol L^{-1}. What is (a) the order of reaction with respect to glucose, (b) the rate constant?

$[C_6H_{12}O_6]/(\text{mmol L}^{-1})$	1.00	1.54	3.12	4.02
Initial rate/$(\text{mol L}^{-1}\ \text{s}^{-1})$	5.0	7.6	15.5	20.0

2. The rate constant for the first-order decomposition of N_2O_5 in the reaction $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ is $k = 3.38\times10^{-5}\ s^{-1}$ at 25°C. What is the half-life of N_2O_5? What will be the total pressure, initially 500 Torr for the pure N_2O_5 vapor, (a) 10 s, (b) 10 min after initiation of the reaction?

3. In a study of the alcohol dehydrogenase catalyzed oxidation of ethanol, the molar concentration of ethanol decreased in a first-order reaction from 220 mmol L^{-1} to 56.0 mmol L^{-1} in 1.22×10^4 s. What is the rate constant of the reaction?

4. In the study of a second-order gas-phase reaction, it was found that the molar concentration of a reactant fell from 220 mmol L^{-1} to 56.0 mmol L^{-1} in 1.22×10^4 s. What is the rate constant of the reaction?

5. A rate constant is 1.78×10^{-4} L mol^{-1} s^{-1} at 19°C and 1.38×10^{-3} L mol^{-1} s^{-1} at 37°C. Evaluate the Arrhenius parameters of the reaction.

6. The activation energy of the first-order decomposition of dinitrogen oxide into N_2 and O is 251 kJ mol^{-1}. The half-life of the reactant is 6.5×10^6 s at 455°C. What will it be at 550°C?

7. Estimate the activation Gibbs energy for the decomposition of urea in the reaction $CO(NH_2)(aq) + 2\ H_2O(l) \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq)$ for which the pseudofirst-order rate constant is $1.2\times10^{-7}\ s^{-1}$ at 60°C and $4.6\times10^{-7}\ s^{-1}$ at 70°C.

8. The reaction $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$ is catalyzed by Br^- ions. If the mechanism is

$H_2O_2 + Br^- \rightarrow H_2O + BrO^-$ (slow)

$BrO^- + H_2O_2 \rightarrow H_2O + O_2 + Br^-$ (fast)

Give the predicted order of the reaction with respect to various participants.

9. The reaction mechanism

$A_2 \leftrightarrows A + A$ (fast)

$A + B \rightarrow P$ (slow)

involves an intermediate A. Deduce the rate law for the formation of P.

10. The condensation reaction of acetone, $(CH_3)_2CO$ (propanone), in aqueous solution is catalyzed by bases, B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$. The carbanion then reacts with a molecule of acetone to give the product. A simplified version of the mechanism is

(1) $AH + B \rightarrow BH^+ + A^-$

(2) $A^- + BH^+ \rightarrow AH + B$

(3) $A^- + HA \rightarrow$ product

where AH stands for acetone and A^- its carbanion. Use the steady-state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.