

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?

$[\text{C}_6\text{H}_{12}\text{O}_6]/(\text{mmol L}^{-1})$	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 $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is $k = 3.38 \times 10^{-5} \text{ s}^{-1}$ 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 $1.22 \times 10^4 \text{ s}$. What is the rate constant of the reaction?

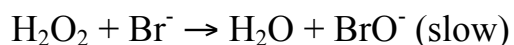
4. In the study of a second-order gas-phase reaction, it was found that the molar concentration of a reactant fell from 220 mmol L^{-1} to 56.0 mmol L^{-1} in $1.22 \times 10^4 \text{ s}$. What is the rate constant of the reaction?

5. A rate constant is $1.78 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 19°C and $1.38 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ 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 $6.5 \times 10^6 \text{ s}$ at 455°C . What will it be at 550°C ?

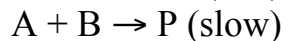
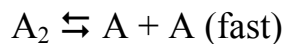
7. Estimate the activation Gibbs energy for the decomposition of urea in the reaction $\text{CO}(\text{NH}_2)(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NH}_4^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ for which the pseudofirst-order rate constant is $1.2 \times 10^{-7} \text{ s}^{-1}$ at 60°C and $4.6 \times 10^{-7} \text{ s}^{-1}$ at 70°C .

8. The reaction $2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ is catalyzed by Br^- ions. If the mechanism is



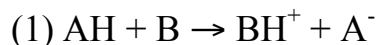
Give the predicted order of the reaction with respect to various participants.

9. The reaction mechanism



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



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.