# 2023 Fall Chemistry 2

## Assignment 3 (Atkins, Focus 7)

(Total 150 pt; Due 2023/11/20 Class)

1. Compounds A and B both decompose by first-order reactions. At 398 K, the rate constant for the decomposition of A is $3.6 \times 10^{-5}$ $s^{-1}$. Separate containers of A and B were prepared, with initial concentrations of 0.120 (mol A)•$L^{-1}$ and 0.240 (mol B)•$L^{-1}$. After 5.0 h, it was found that the concentration of A was 3.0 times the concentration of B. (a) What was the concentration of A at that time? (b) What is the rate constant for the decomposition of B at 398 K? [15 pt]

2. The following mechanism has been proposed for the formation of hydrazine in the overall reaction, $N_2$ (g) + 2 $H_2$ (g) → $N_2H_4$ (g):

   Step 1: $N_2 + H_2 \rightarrow N_2H_2$

   Step 2: $H_2 + N_2H_2 \rightarrow N_2H_4$

   The rate law for the overall reaction is Rate = $k_r[N_2][H_2]^2$. Which step is the slow step? Show your work. [15 pt]

3. (a) From the following mechanism, derive Eq. 1a in Topic 7E, which Michaelis and Menten proposed to represent the rate of formation of products in an enzyme-catalyzed reaction. (b) Show that the rate is independent of substrate concentration at high concentrations of substrate.

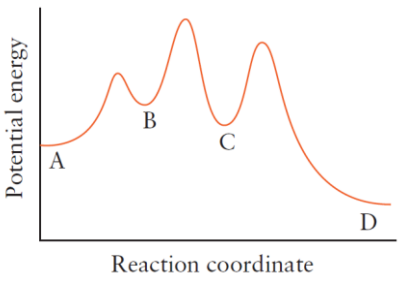
   $E + S \leftrightarrow ES$ $\quad k_1, k_1'$

   $ES \rightarrow E + P$ $\quad k_2$

   where E is the free enzyme, S is the substrate, ES is the enzyme–substrate complex, and P is the product. Note that the steady-state concentration of free enzyme will be equal to the initial concentration of the enzyme less the amount of enzyme that is present in the enzyme–substrate complex: $[E] = [E]_0 - [ES]$. [30 pt]

4. A gas composed of molecules of diameter 0.50 nm takes part in a chemical reaction at 300 K and 1.0 atm with another gas (present in large excess) consisting of molecules of about the same size and mass to form a gas-phase product at 300 K. The activation energy for the reaction is 25 kJ•$mol^{-1}$. Use collision theory to calculate the ratio of the reaction rate at 320 K to that at 300 K. [15 pt]

5. The following schematic reaction profile is for the reaction A → D. (a) Is the overall reaction exothermic or endothermic? Explain your answer. (b) How many intermediates are there? Identify them. (c) Identify each activated complex and reaction intermediate. (d) Which step is rate determining? Explain your answer. (e) Which step is the fastest? Explain your answer. [25 pt]




6. The pre-equilibrium and the steady-state approximations are two different approaches to deriving a rate law from a proposed mechanism. For the following mechanism, determine the rate law (a) by the pre-equilibrium approximation and (b) by the steady-state

approximation. (c) Under what conditions do the two methods give the same answer? (d) What will the rate laws become at high concentrations of $Br_2$? [30 pt]

$CH_3OH + H^+ \leftrightarrow CH_3OH_2^+$ (fast equilibrium)

$CH_3OH_2^+ + Br^- \rightarrow CH_3Br + H_2O$ (slow)

7. The contribution to the destruction of the ozone layer caused by high-flying aircraft has been attributed to the following mechanism:

Step 1: $O_3 + NO \rightarrow NO_2 + O_2$

Step 2: $NO_2 + O \rightarrow NO + O_2$

(a) Write the overall reaction. (b) Write the rate law for each step and indicate its molecularity. (c) What is the reaction intermediate? (d) A catalyst is a substance that accelerates the rate of a reaction and is regenerated in the process. What is the catalyst in the reaction? (See Box 7E.1.) [20 pt]