1. (10+5+5+5 points) Consider the acid/bromide catalyzed disproportionation reaction:

$$2\,H_2O_2(aq) \xrightarrow[H_3O^+]{Br^-} 2\,H_2O(\ell) + O_2(g)\uparrow$$

for which a postulated mechanism is:

$$H_3O^+ + H_2O_2 \xleftrightarrow{K_{eq}} H_3O_2^+ + H_2O \text{ (fast)}$$
$$H_3O_2^+ + Br^- \xrightarrow{k_1} HOBr + H_2O \text{ (slow)}$$
$$HOBr + H_2O_2 \xrightarrow{k_2} H_3O^+ + O_2 + Br^- \text{ (fast)}$$

A. Write the differential rate law in terms of reactants and catalysts.

B. If the overall rate increases by a factor of 4000, calculate the <u>decrease</u> (kJ/mol) in E_a effected by the catalysts.

C. [True or False] If the value of k_2 is ca. 10^{11} $L \cdot mol^{-1} \cdot s^{-1}$, this solution-phase reaction rate is activation-limited. <u>Explain</u>.

D. How is the <u>enthalpy</u> of this highly exothermic reaction affected by the catalysts?

2. (4+6+5 points) The temperature dependence of the iodine clock reaction was measured in a laboratory.

A. From measured reaction times at three temperatures, a graph of ___ _____ vs. _____ yielded a straight line with a slope of -1311 K and an intercept of 1.22.

B. Calculate E_a from this information.

C. Calculate the fraction of collisions with energy sufficient to react at 300K.

3. (10+5+10 points) The mechanism for the decomposition of NO_2Cl is:

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} NO_2 + Cl$$

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

A. By making a steady-state approximation for [Cl], express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2.

B. Graph the concentration of Cl vs. time.

C. Graph $\frac{d[Cl_2]}{dt}$ vs. $[NO_2Cl]$ as expected for high NO_2 concentrations.

4. (10 points) The rate for the reaction

$$OH^-(aq) + NH_4^+(aq) \longrightarrow H_2O(\ell) + NH_3(aq)$$

is first order in both OH^- and NH_4^+ concentractions, and the rate constant k at 20°C is 3.4×10^{10} L mol^{-1} s^{-1}. Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M NH_4Cl solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of 1.0×10^{-5} M.

5. (5+5 points) Certain bacteria use the enzyme penicilinase to decompose penicillin and render it inactive. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5}$ mol L^{-1} and $k_2 = 2 \times 10^3$ s^{-1}.

A. What is the maximum rate of decomposition of penicillin if the enzyme concentration is 6×10^{-7} M?

B. At what substrate concentration will the rate of decomposition be half that calculated in part A?

6. (15 points) Calculate the rate constant for the abstraction reaction, carried out in the gas phase at 800K:

$$\cdot OH + CH_4 \longrightarrow H_2O + \cdot CH_3$$

The activation energy is 32 kJ/mol. The molecular diameters are 1.10 (OH) 2.90 (CH_4) and 1.70 (H_20) Angstroms (1 Å = 10^{-10} M). The steric factor is 0.12 and the enthalpy change is -175 kJ/mol.

$$\bar{C} = \sqrt{\frac{8RT}{\pi\mu}}$$