Chemistry 1B S'99, Exam I RJ Saykally Name _____ 1

1. (5 points each) We demonstrated the highly explosive reaction $2\,H_2 + O_2 \rightarrow 2\,H_2O$, for which the following steps of the chain mechanism are known:

1) $H_2 + O_2 \xrightarrow{k_1} HO_2 + H$

2) $H_2 + HO_2 \xrightarrow{k_2} OH + H_2O$

3) $OH + H_2 \xrightarrow{k_3} H_2O + H$

4) $OH + OH \xrightarrow{k_4} H_2O + O$

5) $M + O_2 \xrightarrow{k_5} O + O + M$ (M is any collision partner)

A. Which reactions are <u>propagation</u> steps? _____

B. Write the differential rate law for elementary step (4) in terms of H_2O production.

C. Show how the rate constant for step (4) can be extracted from a suitable graph (draw and label the graph).

D. The activation energy for step (3) is 42 kJ/mol. What <u>fraction</u> of reactant collisions could lead to products at 1200°C?

E. Experiments show that only ~1 in 10 of the collision that do have $E > E_a$ actually lead to reaction in step (3). Rationalize this (draw structures).

F. Write the steady-state condition for OH radicals in terms of the elementary steps given above.

G. If the activation energy for a given reaction is found by experiment to be zero, how does the reaction rate depend on temperature?

H. Many solid-state explosions occur via a thermal mechanism. Explain how thermal explosions occur.

2. (10 points) The hydrogenation reaction $H_2 + C_2H_4 \rightarrow C_2H_6$ is found to be first-order in both H_2 and C_2H_4. The hard sphere collision cross section is 0.46 nm^2 and the reduced mass for the colliding pair is $\mu = 1.81 \times 10^{-3}$ kg/mole. The measured value of the pre-exponential factor at 628K is $1.24 \times 10^6 \left(\frac{\text{mole}}{\text{liter}}\right)^{-1} s^{-1}$.

   Calculate the steric factor for this reaction. $\left[A = \sigma \left(\frac{8RT}{\pi\mu}\right)^{1/2} N_o\right]$

3. (10 points) The water in a pressure cooker boils at a temperature greater than 100°C because it is under pressure. At this higher temperature, the chemical reactions associated with the cooking of food take place at a greater rate.

   Some food cooks fully in 5 min in a pressure cooker at 112°C and in 10 min in an open pot at 100°C. Calculate the average activation energy for the reactions associated with the cooking of this food.

4. (10 points) Chloromethane decomposes at elevated temperatures according to the reaction

$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

This reaction obeys first-order kinetics. After 340 s at 800 K, a measurement shows that the concentration of C_2H_5Cl has decreased from 0.0098 mol L^{-1} to 0.0016 mol L^{-1}. Calculate the rate constant k at 800 K.

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

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

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

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.

6. (5+5 points) The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 8 \times 10^{-5}$ mol L^{-1} and $k_2 = 6 \times 10^5$ s^{-1}.

A. What is the maximum rate of reaction of carbon dioxide if the enzyme concentration is 5×10^{-6} M?

B. At what CO_2 concentration will the rate of decomposition be 30% of that calculated in part (a)?

7. (5+5 points) The decomposition of hydrogen peroxide $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ catalyzed by H_3O^+ and Br^- proceeds via the following mechanism:

1. $H_3O^+ + H_2O_2 \overset{K_{eq}}{\leftrightarrow} H_3O_2^+ + H_2O$ (fast)

2. $H_3O_2^+ + Br^- \overset{k_2}{\rightarrow} HOBr + H_2O$ (slow)

3. $HOBr + H_2O_2 \overset{k_3}{\rightarrow} H_3O^+ + O_2 + Br^-$ (fast)

A. Derive the overall rate law in terms of O_2 production and H_3O^+, Br^-, and H_2O_2 concentrations.

B. Br^- is a catalyst for this reaction, increasing the reaction rate by 3×10^3 at 298K. By how much does it lower the activation energy from its uncatalyzed value of 76 kJ/mole?