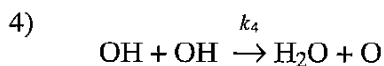
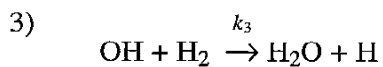
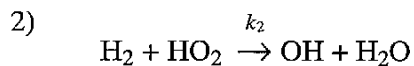
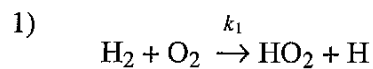


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1. (5 points each) We demonstrated the highly explosive reaction $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$, for which the following steps of the chain mechanism are known:



- A. Which reactions are propagation 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 fraction of reactant collisions could lead to products at 1200°C?

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- 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.

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2. (10 points) The hydrogenation reaction $\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$ 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 $\mu = 1.81 \times 10^{-3} \text{ kg/mole}$. The measured value of the pre-exponential factor at 628K is $1.24 \times 10^6 \left(\frac{\text{mole}}{\text{liter}}\right)^{-1} \text{ s}^{-1}$.

Calculate the steric factor for this reaction.

$$\left[A = \sigma \left(\frac{8RT}{\pi\mu} \right)^{1/2} N_0 \right]$$

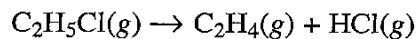
3. (10 points) The water in a pressure cooker boils at a temperature greater than 100°C because it is under pressure. At this higher temperature, the chemical reactions associated with the cooking of food take place at a greater rate.

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.

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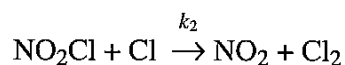
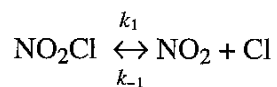
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4. (10 points) Chloromethane decomposes at elevated temperatures according to the reaction



This reaction obeys first-order kinetics. After 340 s at 800 K, a measurement shows that the concentration of $\text{C}_2\text{H}_5\text{Cl}$ has decreased from $0.0098 \text{ mol L}^{-1}$ to $0.0016 \text{ mol L}^{-1}$. Calculate the rate constant k at 800 K.

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



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

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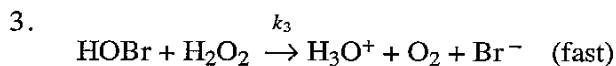
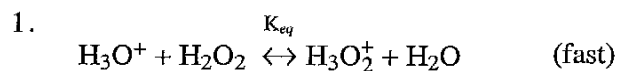
6. (5+5 points) The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 8 \times 10^{-5} \text{ mol L}^{-1}$ and $k_2 = 6 \times 10^5 \text{ s}^{-1}$.

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

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 $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$

catalyzed by H_3O^+ and Br^- proceeds via the following mechanism:



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

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- 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?