CHM 106 Exam I

1. Sulfur hexafluoride is a gas that is frequently used as an electrical insulator (to prevent high voltage arcs) due to its high dielectric strength. However, it can dissociate as shown in the following equilibrium:

$$SF_6(g) \rightleftharpoons SF_4(g) + F_2(g)$$

The fluorine formed through this equilibrium reaction will react with virtually anything it comes in contact with, which limits the usefulness of SF_6 at high temperatures.

a) At 1000 °C, the equilibrium constant for this reaction is 1.79×10^{-8} . If the initial concentration of $[SF_6]_0 = 0.048 \text{ M}$, what are the equilibrium concentrations of all species?

b) Assuming that any appreciable amount of $F_2(g)$ formed will be consumed in reactions with the surroundings, use Le Châtelier's principle to explain why $SF_6(g)$ is a poor choice of insulator at high temperatures.

 $[CO]_0 \pmod{/L}$ $[NO_2]_0 (mol / L)$ Initial rate (mol / $L \cdot s$) 2.52×10^{-4} 0.010 0.010 1.01×10^{-3} 0.020 0.010 2.27×10^{-3} 0.030 0.010 2.52×10^{-4} 0.010 0.020 2.52×10^{-4} 0.010 0.030

2. Initial rate data was collected for the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$:

a) What is the (differential) rate law for this reaction?

b) What is the value of the rate constant?

c) Several mechanisms have been proposed to explain this reaction. Which of the following mechanisms is consistent with the kinetic data? Explain.

Mechanism I:	$\begin{array}{l} \mathrm{NO}_2 + \mathrm{NO}_2 \rightarrow \mathrm{N}_2\mathrm{O}_4 \\ \mathrm{N}_2\mathrm{O}_4 + \mathrm{CO} \rightarrow \mathrm{NO} + \mathrm{CO}_2 + \mathrm{NO}_2 \end{array}$	slow fast
Mechanism II:	$NO_2 + CO \rightarrow NO + CO_2$	slow
Mechanism III:	$\begin{split} & NO_2 + NO_2 \rightarrow N_2O_4 \\ & N_2O_4 + CO \rightarrow N_2O_3 + CO_2 \\ & N_2O_3 \rightarrow NO + NO_2 \end{split}$	slow fast fast

3. Ammonium carbonate, $(NH_4)_2CO_3$, was once used as "smelling salts" to revive the fainted. Ammonium carbonate decomposes to form ammonia, carbon dioxide, and water in the following equilibrium:

$$(NH_4)_2CO_3(s) \rightleftharpoons 2 NH_3(g) + CO_2(g) + H_2O(g)$$

The offensive odor of the ammonia is responsible for the stimulation of respiration and a return of consciousness.

a) What is the equilibrium expression for this reaction?

b) A rigid flask containing excess solid ammonium carbonate at room temperature (298 K) is evacuated and the system is allowed to come to equilibrium. At equilibrium, the total pressure inside the flask is 0.0681 atm. What are the equilibrium partial pressures of all the products?

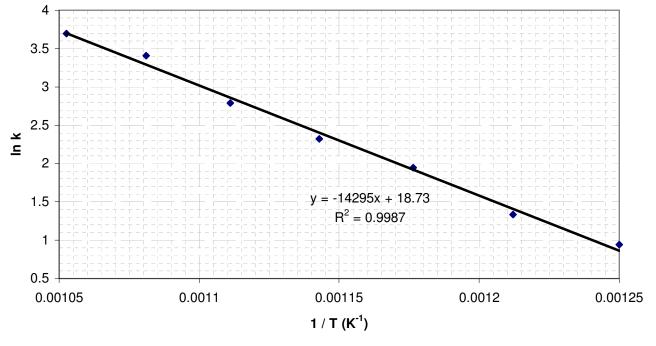
c) What is the value of the equilibrium constant K_p ?

d) What is the minimum volume of a vessel necessary for a 0.10 g sample of $(NH_4)_2CO_3$ to completely decompose?

4. In the gas phase, chlorobenzene reacts with hydrogen sulfide to form thiophenol and hydrogen chloride:

$$PhCl(g) + H_2S(g) \rightarrow PhSH(g) + HCl(g)$$

Kinetic studies were performed on this system and a plot of the natural log of the rate constant versus the reciprocal of the temperature was prepared:



a) Calculate the activation energy for this reaction.

b) Suppose that a catalyst is discovered that changes the activation energy of this reaction to 100 kJ / mol. Will this catalyst speed up or slow down the reaction? Explain.

5. Drug metabolism in the body can often be analyzed using a simple kinetic model. For a general model of drug metabolism, the active drug (A) is converted into inactive metabolites (B):

$$A(aq) \rightarrow B(aq)$$

Suppose that kinetics experiments are performed on a drug undergoing clinical trials. A plot of the natural log of the concentration of the drug in the bloodstream versus time is linear. It takes 14.5 hours for half of the drug to be eliminated.

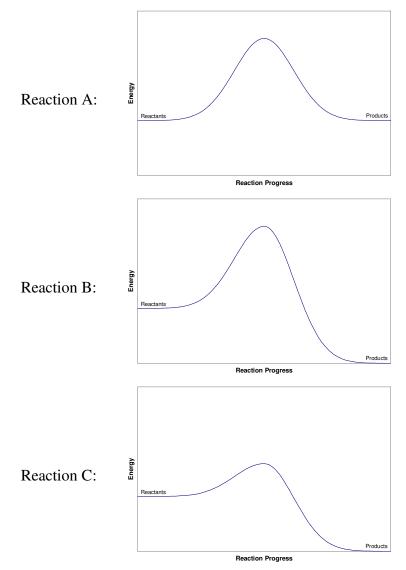
a) What is the integrated rate law for this reaction?

- b) What is the order of the reaction with respect to the drug?
- c) What is the value of the rate constant for this reaction?

d) How long does it take for a dose of $[A]_0 = 7.14 \times 10^{-6} \text{ M}$ to be 95% metabolized?

For the remaining questions, circle the letter that corresponds to the best answer.

6. The reaction progress diagrams for several reactions are given:



Which of the following statements are *true*?

- I. Reaction B and reaction C have the same activation energy.
- **II**. Reaction C will react faster than reaction A or reaction B.
- **III**. Reaction B may be the same as reaction A, but with a catalyst added.
- IV. Reaction C may be the same as reaction B, but with a catalyst added.
 - (A) **II** only
 - (B) I and III
 - (C) I and IV
 - (D) II and IV
 - (E) all of the above

For questions 7 - 10, consider the following disturbances to systems at equilibrium and predict the nature of the shift in the equilibrium position.

7. $H^+(aq)$ is added to $2 In^{3+}(aq) + H_3PO_2(aq) + H_2O(l) \implies 2 In^{2+}(aq) + H_3PO_3(aq) + 2H^+(aq)$

- (A) The equilibrium will shift left.
- (B) The equilibrium will shift right.
- (C) The equilibrium position will not change.

8. $UO_2(s)$ is removed from the system $UO_2(s) + 4 HF(g) \Longrightarrow UF_4(g) + 2 H_2O(g)$

- (A) The equilibrium will shift left.
- (B) The equilibrium will shift right.
- (C) The equilibrium position will not change.

9. The volume is decreased on the system $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

- (A) The equilibrium will shift left.
- (B) The equilibrium will shift right.
- (C) The equilibrium position will not change.
- 10. The endothermic reaction $N_2(g) + 2 H_2(g) \rightleftharpoons N_2H_4(g)$ is heated
 - (A) The equilibrium will shift left.
 - (B) The equilibrium will shift right.
 - (C) The equilibrium position will not change.
- 11. Which of the following statements are *false*?
- I. Termolecular elementary steps are rare because three molecules seldom collide at the same time.
- **II**. Molecules react whenever they collide.
- **III**. The activation energy of a reaction determines whether it is exothermic or endothermic.
- **IV**. The activation energy of a reaction determines how fast the reaction proceeds.
 - (A) **I** only
 - (B) **III** only
 - (C) **IV** only
 - (D) I and IV
 - (E) **II** and **III**

12. Under what conditions will the following reaction proceed left to reach equilibrium?

 $\operatorname{Cl}_2(g) + 3 \operatorname{F}_2(g) \rightleftharpoons 2 \operatorname{ClF}_3(g)$

(A) K > 1(B) K < 1(C) Q > K(D) Q < K

13. What is the order of the reaction below?

 $2 \operatorname{NH}_3(g) + 3 \operatorname{O}_2(g) \rightarrow 2 \operatorname{NO}_2(g) + 2 \operatorname{H}_2\operatorname{O}(g)$

- (A) First order
- (B) Second order
- (C) Third order
- (D) Fifth order
- (E) The order cannot be determined from the data given

14. For the reaction $2 N_2O(g) \rightarrow 4 NO_2(g) + O_2(g)$, the rate of formation of $NO_2(g)$ is 5.78 mol / L · s. Therefore, the rate of appearance of $O_2(g)$ is:

- (A) $23.1 \text{ mol} / \text{L} \cdot \text{s}$
- (B) 2.89 mol / L · s
- $(C) \qquad 5.78 \text{ mol} \, / \, L \cdot s$
- (D) $1.45 \text{ mol} / \text{L} \cdot \text{s}$

15. Given that K >> 1 for a chemical reaction, which of the following are *true*?

- I. The equilibrium would be achieved rapidly.
- **II**. The equilibrium would be achieved slowly.
- **III**. Product concentrations will be greater than reactant concentrations at equilibrium.
- **IV**. Reactant concentrations will be greater than product concentrations at equilibrium.
- V. The concentrations of reactants and products should be about equal.
 - (A) I and III
 - (B) II and IV
 - (C) I and V
 - (D) **III** only
 - (E) **IV** only

Equations and Constants

$$PV = nRT \qquad \ln k = -\frac{E_{a}}{R}\frac{1}{T} + \ln A$$

$$\ln [A] = -kt + \ln [A]_{0} \qquad \ln \frac{k_{1}}{k_{2}} = -\frac{E_{a}}{R}\left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_{0}} \qquad ax^{2} + bx + c = 0$$

$$[A] = -kt + [A]_{0} \qquad x = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2a}$$

$$K_{p} = K(RT)^{\Delta n}$$

 $R = 8.314 \text{ J} / \text{mol} \cdot \text{K} = 0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$