### for the reaction? a. 8.06x10<sup>-4</sup> s<sup>-1</sup>. b. 8.06x10<sup>-4</sup>M<sup>-1</sup>s<sup>-1</sup> c. 5.59x10<sup>-3</sup> s<sup>-1</sup> Answer d. 5.59x10<sup>-3</sup> M<sup>-1</sup>s<sup>-1</sup> 2. For the reaction $A + B \rightarrow 2C$ , which proceeds by a single-step bimolecular elementary process. a. $t_{1/2} = 0.693/k$ . b. the rate of appearance of C = -rate of disappearance of A. c. rate of the reaction = k[A][B]. Answer d. $\ln[A]_t = -kt + \ln[A]_0$ 3. The volume of the reaction vessel containing an equilibrium mixture in the reaction $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is increased. When equilibrium is reestablished, a. the amount of Cl<sub>2</sub> will have increased. b. the amount of SO<sub>2</sub> will have decreased. c. the amounts of SO<sub>2</sub> and Cl<sub>2</sub> will have remained the same. Answer d. the amount of SO<sub>2</sub>Cl<sub>2</sub> will have increased. 4. For the reaction CO (g) + H<sub>2</sub>O (g) $\rightleftharpoons$ H<sub>2</sub> (g) + CO<sub>2</sub>(g) at 1000K, K<sub>c</sub> = 0.66 and $\Delta$ H<sup>0</sup> = -42 kJ. After an initial equilibrium is established in a 1.00 L container, the equilibrium amount of $H_2$ can be increased by, a. adding a catalyst. b. increasing the temperature. c. transferring the mixture to a 10.0 L container. Answer d. some way other than (a), (b), or (c). 5. Which of the acids below would have the *weakest conjugate base*? a. CH<sub>3</sub>COOH (acetic acid, $K_a = 1.8 \times 10^{-5}$ ) b. HCl (hydrochloric acid, $K_a = 1000$ ). c. HOCI (hypochlorous acid, $K_a = 3.0 \times 10^{-8}$ ). d. $HCO_2H$ (formic acid, $K_a = 1.8 \times 10^{-4}$ ) Answer

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions. I have intentionally left a great deal of space for each

1. The reaction  $A \rightarrow$  products has been determined to be first order in A. The reaction is run

with  $[A]_0 = 0.20$  M and is found to have a half-life of 124 seconds. What is the rate constant

problem. I do not expect each problem to take up all of the space provided!

**Bonus (5 points).** I wrote a concentration on the board at the start of class one day and said it would be an answer on the exam. Write that concentration here with the correct units.

### Chem 120 Exam 4, Ch 14, 15 and a little 16 100 Points

Part 0: Warmup. 4 points each

Name\_\_\_\_\_

December 4, 2008

#### Part I: Complete all of problems 6-8.

6. Complete the following reaction and identify the conjugate acid-base pairs. For each pair, identify the acid and the conjugate base. (8 points)

HCI (aq) + NH<sub>3</sub> (aq) *≥* 

7. Briefly describe what we mean when we say that a system is *at equilibrium*. Why do we use a double-headed arrow (like *≥*) when we write these reactions? (12 points)

8. How does a catalyst impact the rate of a reaction and the extent to which the reaction goes to completion? (8 points)

# Part II Kinetics. Answer two (2) of problems 9-11. Clearly mark the problems you do not want graded. 14 points each.

9. The initial rate data below is for the reduction of mercury with oxalate ion. Using this information, determine the rate law for the reaction as well as the rate constant (with appropriate units).

| Experiment | [HgCl <sub>2</sub> ], M | [C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> ], M | Initial Rate, M min <sup>-1</sup> |
|------------|-------------------------|---|-----------------------------------|
| 1          | 0.105                   | 0.300   | 7.18x10⁻⁵                         |
| 2          | 0.052                   | 0.300   | 3.56x10⁻⁵                         |
| 3          | 0.208                   | 0.600   | 5.69x10 <sup>-4</sup>             |

 $2 \text{ HgCl}_2 + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{ Cl}^- + 2 \text{ CO}_2 + \text{Hg}_2\text{Cl}_2$ 

10. You are investigating the reaction of a newly discovered cancer drug named LAMPROCKS (abbreviated L). You have been charged with determining the rate law for the decomposition of LAMPROCKS into its two components, LAMP and ROCKS. The rate only depends on L and no other reactants. You have collected the following data and made the plots below. Based on this data, what is the <u>rate law</u> for this reaction and what is the value of the <u>rate constant</u> with the appropriate units? *Justify your choice for the rate law and show your work for the k determination*.



- 11. For the reaction A + 2B  $\rightarrow$  C + D, the rate law is: rate = k[A][B].
  - a. Show that the following mechanism is consistent with the stoichiometry of the overall reaction and with the rate law.

$$\begin{array}{rcl} A+B & \stackrel{K_1}{\rightarrow} & W \text{ (slow)} \\ \\ W+B & \stackrel{K_2}{\rightarrow} & C+D \text{ (fast)} \end{array}$$

b. Show that the following mechanism is consistent with the stoichiometry of the overall reaction, but <u>not</u> with the rate law.

$$\begin{array}{ccc} 2 \ B & \stackrel{k_1}{\underset{k_{-1}}{\xrightarrow{}}} & B_2 \ (fast) \\ A + B_2 & \stackrel{k_2}{\rightarrow} & C + D \ (slow) \end{array}$$

# Part III Equilibrium. Answer two (2) of problems 12-14. Clearly mark the problems you do not want graded. 14 points each.

12. For the equilibrium below,  $K_c = 2.0 \times 10^{-6}$ . What is the equilibrium concentration of oxygen (in moles/L) if 0.20 mol CO<sub>2</sub> and 0.10 mol CO were initially placed into a 0.50 L vessel and the system is allowed to come to equilibrium?

 $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ 

13. In the gas phase, iodine reacts with cyclopentane to produce cyclopentadiene and hydrogen iodide. Explain how each of the following affects the amount of HI (g) present in the equilibrium mixture in the reaction:

 $I_2(g) + C_5H_8(g) \rightleftharpoons C_5H_6(g) + 2 HI(g)$   $\Delta H^\circ = +92.5 \text{ kJ}$ 

a. raising the temperature of the mixture.

b. doubling the volume of the container holding the mixture.

c. introducing more  $C_5H_6(g)$ .

14. For the reaction  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$  occurring at a temperature 1000K, K<sub>c</sub> =100. If 0.455 mol SO<sub>2</sub>, 0.183 mol O<sub>2</sub>, and 0.568 mol SO<sub>3</sub> are introduced simultaneously into a 1.90 L vessel at 1000K, is the system at equilibrium? If not, in which direction will a net change occur? *NOTE: you do not need to calculate the equilibrium concentrations, just clearly justify your answers.* 

#### **Possibly Useful Information**

| slope = m = $\frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$ | y = mx + b  | R = 0.08206 L atm mol <sup>-1</sup> K <sup>-1</sup> |
|---|---|---|
| pH + pOH = 14   | $K_a K_b = K_w$   | $K_p = K_c(RT)^{\Delta n}$                          |
| $k = Ae^{-E_{a/RT}}$  | $\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$ | $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$            |
| rate = k[A] <sup>1</sup>  | $[A]_t = -kt + [A]_0$   | $t_{1/2} = [A]_0/2k$                                |
| rate = k[A] <sup>2</sup>  | $ln[A]_t = -kt + ln[A]_0$   | $t_{1/2} = 1/(k[A]_0)$                              |
| rate = k[A] <sup>0</sup>  | $\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$    | t <sub>1/2</sub> = 0.693/k                          |



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