| Chem 130 | Name |
|----------------------|------|
| Exam 3, Ch 14 and 15 | |
| 100 Points | |

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.

December 7, 2011

| Part 0: Warmup. 4 points eac | points eac | 4 p | /armup. | : W | rt 0: | Pa |
|------------------------------|------------|-----|---------|-----|-------|----|
|------------------------------|------------|-----|---------|-----|-------|----|

| 1. | Half-life is independent of | f initial concentration for | reactions : |
|----|------------------------------------|---|-------------|
| | a. zero order | d. no | |
| | b. first order | e. all | |
| | c. second order | | Answer |
| 2. | • | in vessel that contains an equile $\underline{g}(g)$ is increased. When equilib | |
| | a. the amount of Cl ₂ w | | |
| | b. the amount of SO ₂ v | ill have decreased. | Answer |
| | c. the amounts of SO ₂ | e same. | |
| | d. the amounts of all S | O_2 , Cl_2 , and SO_2Cl_2 will have d | lecreased |

- 3. For the reaction $CO(g) + 2H_2(g) \gtrsim CH_3OH(g)$ $K_c = 14.5$. If 5.00 mol CO, 2.00 mol CO, and 3.00 mol of CH_3OH are brought together and allowed to react, which of the following describes the composition of the system at equilibrium?
 - a. Some CO and H_2 will have been consumed to make more CH_3OH . Answer _____
 - Some CH₃OH will have been consumed to make more CO and H₂
 - c. The amounts of CO, H₂, and CH₃OH will be unchanged from their initial values.
 - d. There is not enough information to determine the equilibrium composition.

Part I: Complete problem 4. (10 points)

4. The decomposition of hydrogen peroxide (H₂O₂) to liquid water and oxygen gas is a <u>spontaneous</u> process, but occurs <u>slowly</u>, allowing for a reasonable shelf-life for peroxide solutions. In the presence of a catalyst (like the iron in your blood), the decomposition is much <u>more rapid</u>. Draw and correctly label reaction coordinate diagrams that represent each of the two situations and describe how each diagram reflects the thermodynamics and kinetics of the situation.

Part II Kinetics. Answer three (3) of problems 5-8. Clearly mark the problems you do not want graded. 15 points each. (13 points each)

Use the tabulated data below for problems 5 and 6. The data corresponds to the reaction below and shows dependence of concentration of A on time in experiments run at three temperatures.

$$2A \rightarrow B + C$$

| | T = 298 K | T = 348 K | T = 398 K |
|------------|-----------|-----------|-----------|
| Time (sec) | [A] (M) | [A] (M) | [A] (M) |
| 0 | 0.1000 | 0.1000 | 0.1000 |
| 1 | 0.0999 | 0.0991 | 0.0940 |
| 2 | 0.0999 | 0.0983 | 0.0883 |
| 8 | 0.0995 | 0.0932 | 0.0609 |
| 32 | 0.0980 | 0.0755 | 0.0137 |

5. Consider the data above. Clearly <u>describe</u> how the data could be used to determine the order for the reaction in A. No calculations are necessary. Feel free to include appropriate diagrams.

6. Consider the data above. Assuming you know the reaction to be first order in A, <u>describe</u> how you could determine the activation energy for the reaction. No calculations are necessary. Feel free to include appropriate diagrams.

7. The reaction $I^-(aq) + OCI^-(aq) \rightarrow IO^-(aq) + CI^-(aq)$ was studied and the data below were obtained. Determine the rate law and the value of the rate constant for this reaction.

| [I ⁻] ₀ (mol/L) | [OCl ⁻] ₀ (mol/L) | Initial Rate (mol/Ls) |
|--|--|-----------------------|
| 0.12 | 0.18 | 0.0791 |
| 0.060 | 0.18 | 0.0395 |
| 0.030 | 0.090 | 0.00988 |
| 0.24 | 0.090 | 0.0791 |

8. Experiment has shown that the rate law for the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ is Rate = k[NO][Cl₂]. One proposed mechanism for this process is shown below, with the second step being rate-determining. Is this a reasonable mechanism for the reaction? Justify your decision.

$$\begin{array}{cccc} \text{NO} + \text{Cl}_2 & \overset{k_1}{\rightleftharpoons} & \text{NOCl}_2 \text{ (fast)} \\ \\ \text{NOCl}_2 + \text{NO} & \xrightarrow{} & \text{2NOCl (slow)} \end{array}$$

Part III Equilibrium. Answer three (3) of problems 9-12. Clearly mark the problems you do not want graded. (13 points each)

9. What do we mean when we say a system has *come to equilibrium*? Describe the equilibrium condition and why we don't use a single headed arrow when we write equilibria. What does a small equilibrium constant mean in terms of thermodynamics?

10. Consider the reaction below. If the initial concentrations of H₂, F₂, and HF are 0.0100M, 1.25 M, and 2.21 M, respectively, is the system at equilibrium? If not, which way will the reaction go to achieve the equilibrium condition? Set up, but do not complete the calculation you would use to determine the equilibrium concentrations of each of the species in the reaction. You DO NOT need to arrive at a numerical answer, just get to the point where you have one algebraic expression you could solve, given additional time. Be sure to tell me what you would do with the result of your calculation.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$
 K = 115

11. Suppose the reaction system below has already reached equilibrium. Predict the effect of the following changes on the system. Justify your predictions with a brief statement.

$$UO_2(s) + 4HF(g) \rightleftharpoons UF_4(g) + 2H_2O(g)$$

- a. More UO_2 is added to the system.
- b. The reaction is performed in a glass reaction vessel and the HF reacts with the glass.
- c. Water vapor is removed.
- d. The volume is increased.
- 12. You have been tasked with determining the equilibrium constant for the reaction of H_2 and S_2 gases to produce hydrogen sulfide. A mixture of 1.00 g H_2 and 1.00 g H_2 S in a 0.500 L flask comes to equilibrium at 1670 K. At equilibrium, there is 8.00 x 10⁻⁶ mol of S_2 present. What are the values for K_c and K_p at this temperature?

Possibly Useful Information

| slope = m = $\frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$ | $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ | R = 0.08206 L atm mol ⁻¹ K ⁻¹ R = 8.314 J mol ⁻¹ K ⁻¹ |
|---|---|--|
| pV = nRT | $\Delta G = -RTInK$ | $K_p = K_c(RT)^{\Delta n}$ |
| $k = Ae^{-E_{a/RT}}$ | $\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$ | $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ |
| rate = k[A] ¹ | $[A]_t = -kt + [A]_0$ | $t_{1/2} = [A]_0/2k$ |
| rate = k[A] ² | $ln[A]_t = -kt + ln[A]_0$ | $t_{1/2} = 1/(k[A]_0)$ |
| rate = k[A] ⁰ | $\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$ | $t_{1/2} = 0.693/k$ |

| 1 | | | | | | | | | | | | | | | | | 18 |
|------------------------------|---------------------|----------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|---------------------|---------------------|
| 1A | | | | | | | | | | | | | | | | | 8A |
| 1 H 1.00794 | 2 2A | | | | | | | | | | | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A | 2 He 4.00260 |
| 3 Li 6.941 | 4 Be 9.01218 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984 | 10 Ne 20.1797 |
| 11 Na 22.9898 | 12 Mg 24.3050 | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 | 9 -8B- | 10 | 11 1B | 12 2B | 13 Al 26.9815 | 14 Si 28.0855 | 15 P 30.9738 | 16 S 32.066 | 17 Cl 35.4527 | 18 Ar 39.948 |
| 19 K 39.0983 | 20 Ca 40.078 | 21 Sc 44.9559 | 22 Ti 47.88 | 23 V 50.9415 | 24 Cr 51.9961 | 25 Mn 54.9381 | 26 Fe 55.847 | 27 Co 58.9332 | 28 Ni 58.693 | 29 Cu 63.546 | 30 Zn 65.39 | 31 Ga 69.723 | 32 Ge 72.61 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 |
| 37 Rb 85,4678 | 38 Sr 87.62 | 39 Y 88.9059 | 40 Zr 91.224 | 41 Nb 92.9064 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.906 | 46 Pd 106.42 | 47 Ag 107.868 | 48 Cd 112.411 | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.757 | 52 Te 127.60 | 53 I 126.904 | 54 Xe 131.29 |
| 55 Cs 132.905 | 56 Ba 137.327 | 57 *La 138.906 | 72 Hf 178.49 | 73 Ta 180.948 | 74 W 183.84 | 75 Re 186.207 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.967 | 80 Hg 200.59 | 81 Tl 204.383 | 82 Pb 207.2 | 83 Bi 208.980 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra 226.025 | 89 †Ac 227.028 | 104 Rf (261) | 105 Db (262) | 106 Sg (266) | 107 Bh (264) | 108 Hs (277) | 109 Mt (268) | 110 Ds (271) | 111 Rg (272) | | | | | | | |
| *Lanthanide series | | | | | | | | | 1000000 | | | | | | | | |
| [†] Actinide series | | | | 90 Th 232.038 | 91 Pa 231.036 | 92 U 238.029 | 93 Np 237.048 | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (262) |

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