Chemistry 1212NameKEYThursday March 5, 2020Exam #2

Write very clearly and <u>show all of your work</u> for partial credit. A list of equations and constants as well as a periodic table are on the last two pages of your exam.

1.(20 points) Fill in the space with the correct response.

- (a) Write the equilibrium expression for:  $2KClO_{3(s)} \leftrightarrow 3O_{2(g)} + 2KCl_{(s)}$
- (b) Is  $K_p = K_c$  for the reaction above? Yes or No
- (c) If the half-life for a first order reaction is 410s and  $[A]_0 = 1.00 \text{ M}$  what is k?

$$t_{\frac{1}{2}} = \frac{0.693}{k} \to 4.1 \times 10^2 \, s = \frac{0.693}{k} \to \boxed{k = 1.7 \times 10^{-3} \, s^{-1}}$$

- (d) What are the units for the rate constant, k, if the reaction is  $21^{st}$  order?
- (e) How is the rate of consumption of O<sub>2</sub> related to the rate of production of NO?  $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$

(f) What is the order of the reaction if you get a linear plot from ln[concentration] versus time?

(g) How does K<sub>c</sub> change if we multiple it by the chemical reaction by 4?

(h) What is the molecularity of an elementary step which contains one reactant?

(i) Circle the correct response. Will the rate determining step have a bigger or smaller peak in the reaction profile?

(j) Circle the correct response. If the reaction must go in the reverse direction to reach equilibrium then Q is either: greater than, less than, or equal to K.

2. (20 points) The following data were obtained for the reaction:

 $-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t}$ 

 $K_{c}' = K_{c}^{4}$ 

 $1^{st}$ 

unimolecular

 $K_c = \left[ O_{2(g)} \right]$ No

 $M^{-20}s^{-1}$ 

 $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$ 

| [NO] (mol/L) | [Cl <sub>2</sub> ] (mol/L) | Initial Rate (mol/L·s) |
|--------------|----------------------------|------------------------|
| 0.13         | 0.20                       | 0.010                  |
| 0.26         | 0.20                       | 0.040                  |
| 0.13         | 0.10                       | 0.0050                 |

(a) Determine the rate law. Show your work.

Comparison between experiments 1 & 2

$$\frac{rate_1}{rate_2} = \frac{0.010}{0.040} = \frac{\cancel{k}[NO]_1^m [Cl_2]_1^n}{\cancel{k}[NO]_2^m [Cl_2]_2^n} = \left(\frac{0.13}{0.26}\right)^m \left(\frac{0.20}{0.20}\right)^n$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^m \to m = 2$$
(3pts)

Comparison between experiments 1 & 3

$$\frac{rate_{1}}{rate_{3}} = \frac{0.010}{0.0050} = \frac{\cancel{k}[NO]_{1}^{2}[Cl_{2}]_{1}^{n}}{\cancel{k}[NO]_{3}^{2}[Cl_{2}]_{3}^{n}} = \left(\frac{0.13}{0.13}\right)^{2} \left(\frac{0.20}{0.10}\right)^{n} (3pts)$$

$$2 = (2)^{n} \rightarrow n = 1$$

$$rate = k[NO]^{2}[Cl_{2}] \qquad (2pts)$$

(b) What is the overall order of the reaction?  $2+1 = \boxed{3}$  (2*pts*)

(c) Determine the rate constant (with correct units).

$$rate = k [NO]^{2} [Cl_{2}]$$

$$0.010 \frac{mol}{L \cdot s} = k \left[ 0.13 \frac{mol}{L} \right]^{2} \left[ 0.20 \frac{mol}{L} \right] \rightarrow k = \boxed{3.0 \frac{L^{2}}{mol^{2} \cdot s}}$$
(5pts)

(d) What would be the initial rate for an experiment when both reactants are 0.12M?

$$rate = 3.0 \frac{L^2}{mol^2 \cdot s} [NO]^2 [O_2]$$

$$rate = 3.0 \frac{L^2}{mol^2 \cdot s} \left[ 0.12 \frac{mol}{L} \right]^2 \left[ 0.12 \frac{mol}{L} \right] = \boxed{0.0052 \frac{mol}{L \cdot s}}$$
(5pts)

3. (30 points) For the mechanism below:

step 1:  $A \rightarrow B + C$  (fast) step 2:  $B + C \rightarrow D + B + E$  (slow) step 3:  $D + C \rightarrow 2B$ (fast)

a. write the rate law for the elementary steps (6 points)

step 1:  $rate_1 = k_1[A]$ step 2:  $rate_2 = k_2[B][C]$ step 3:  $rate_3 = k_3[D][C]$ 

b. determine the molecularity of each elementary step (3 points)

step 1: unimolecular

step 2: bimolecular

step 3: bimolecular

c. determine the rate law for the reaction (7 points)

$$rate_1 = k_1[A] = k_{-1}[B][C] \quad 3pts$$

$$rate_{1} = [B][C] = \frac{k_{1}}{k_{-1}}[A] \quad 1pt$$

$$rate_2 = k_2[B][C] = \frac{\kappa_2 \kappa_1}{k_{-1}}[A] \rightarrow rate = K[A] \quad 3pts$$

d. identify the reaction intermediate(s). (4 points)

$$C\&D$$

e. draw the reaction profile indicating the location of each species, transition state, and activation energy (10 points)



Reaction Coordinate

2 pts for axes labels, 4 pts for species labels, 2 pts for TS, 2pts for  $E_{a1} < E_{a2}$ , 2pts for plot

4. (16 points) At 1400K,  $K_c = 2.5 \times 10^{-3}$  for the reaction below. A 10.0 L reaction vessel at 1400K contains 2.0 mol of CH<sub>4</sub>, 3.0 mol of CS<sub>2</sub>, 3.0 mol of H<sub>2</sub>, and 4.0 mol of H<sub>2</sub>S. Is the reaction mixture at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium? What is the K<sub>p</sub>?

$$CH_{4(g)} + 2H_2S_{(g)} \leftrightarrow CS_{2(g)} + 4H_{2(g)}$$

$$Q = \frac{\left[CS_{2}\right]\left[H_{2}\right]^{4}}{\left[CH_{4}\right]\left[H_{2}S\right]^{2}} \quad (2\,pts)$$

$$\left[CH_{4}\right] = \frac{2.0\,mol}{10.0\,L} = 0.20M \quad \left[H_{2}\right] = 0.30M \quad \left[C_{2}S\right] = 0.30M \quad \left[H_{2}S\right] = 0.40M \quad (3\,pts)$$

$$Q = \frac{0.30^{5}}{0.20 \times 0.40^{2}} = 0.0759 > 0.0025 \quad (2\,pts)$$

$$Q > K \therefore \text{ rxn proceeds toward reactants/reverse/to the left} \quad (3\,pts)$$

$$K_{p} = K_{c} \left(RT\right)^{\Delta n} \quad (1\,pt) \quad \Delta n = 5 - 3 = 2 \quad (1\,pt)$$

$$K_{p} = K_{c} \left(RT\right)^{\Delta n} = 2.5 \times 10^{-3} \left(0.0821 \frac{L \times atm}{mol \times K} \times 1400K\right)^{2} = \boxed{33} \quad (3\,pts)$$

5. Sum14 (14 points) Does the amount of chlorine gas increase, decrease, or remain the same for the following changes? Like inclass exercises

|                            | $2NO_{(g)} + Cl_{2(g)} \leftrightarrow 2NOCl_{(g)}$ | $\Delta H^{\circ} = -65  kJ_{mol}$ |
|----------------------------|---|------------------------------------|
| (a.) T is increased        |   | increase                           |
| (b.) V is decreased        |   | decrease                           |
| (c.) Neon gas is added     |   | remain the same                    |
| (d.) Catalyst is removed   |   | remain the same                    |
| (e.) Nitrogen dioxide gas  | s is removed  | remain the same                    |
| (f.) P is decreased        |   | increase                           |
| (g.) Nitrogen oxide gas is | s added   | decrease                           |