CHEMISTRY 104-4
Prof. Treichel
March 21, 2006

NAME Key

Section _____ T.A._____

EXAM 2

1. This exam has 6 pages. If a page is missing, take the exam to a proctor immediately.

2. PRINT your name now at the top of this page and your name or initials at the top of the remaining pages.

3. **Work must be shown for mathematical problems.** If a correct answer is given without any work, points will be deducted.

4. **Whenever appropriate, include units with numerical answers. All answers should have the correct number of significant figures.**

5. Points for each question are indicated.

6. The exam should be completed in 75 minutes. Budget your time for each question. Check your work after completing the exam.

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Page 3 kinetics/equilibrium		/24
Page 4 equilibrium		/27
Page 5 kinetics problem		/12
Page 6 equilibrium problem		/12
Total		/102

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Part I. (27 pts) Short answers. Fill in the correct answer in the blank space.

1. The decomposition of NO_2 at high temperature, $NO_2(g) \rightarrow NO(g) + 1/2\ O_2(g)$ is second order in reactant concentration. What are the units for the rate constant k in the rate law?

$\frac{L}{mol \cdot time}$

2. You can prove graphically that decomposition of NO_2 is second order. What graph of data gives a straight line?

$\frac{1}{[NO_2]}$ vs. t

3. When $[NO_2] = 0.16$ mol/L the rate of decomposition, $\Delta[NO_2]/\Delta t$, $= -8.8 \times 10^{-2}$ mol/L min. What is value of the rate constant k?

$3.4\ \frac{L}{mol \cdot min}$

$-k = \frac{rate}{[NO_2]^2} = \frac{+8.8 \times 10^{-2}}{[0.16]^2}$

4. When $[NO_2] = 0.16$ mol/L the rate of decomposition, $[\Delta NO_2]/\Delta t$, $= -8.8 \times 10^{-2}$ mol/L min. What is the rate of formation of O_2?

$+4.4 \times 10^{-2}\ \frac{mol}{L \cdot min}$

$-\frac{\Delta[NO_2]}{\Delta t} = \frac{2\Delta[O_2]}{\Delta t}$

5. If $[NO_2]$ is decreased to 0.080 mol/L (1/2 of the value in Q3) what will be the value for $\Delta[NO_2]/\Delta t$?

$-2.2 \times 10^{-2}\ \frac{mol}{L \cdot min}$

$\frac{1}{4}$ of -8.8×10^{-2}

6. The radioactivity of a sample of iodine-131 decreases from 1.8×10^4 dpm to 4.5×10^3 dpm over 16 days. What is the half-life of this isotope?

8 days

2 half-lives $\Rightarrow$ 16 d.

7. Data for the reaction $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$ are given in the table. What is the rate law for the reaction?

$rate = k[SO_2]^2$

Experiment No.	$[SO_2]$, mol/L	$[O_2]$, mol/L	Initial rate, mol/L sec
1 (x 2.5)	2.0×10^{-2}	2.0×10^{-2}	2.4×10^{-2} (x $(2.5)^2$)
2	5.0×10^{-2} (x 1/2)	2.0×10^{-2}	0.15
3	2.0×10^{-2}	1.0×10^{-2} (no chg)	2.4×10^{-2}

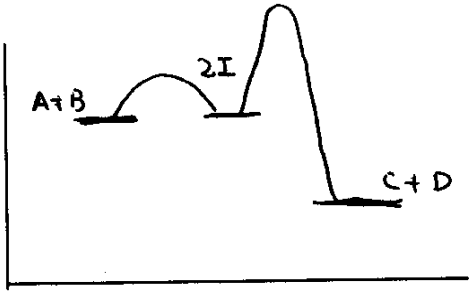
8. What is the rate law for a reaction with a mechanism:

step 1: A + B $\rightleftharpoons$ 2 I (fast equil, energy neutral)

step 2: 2 I $\rightarrow$ C + D (slow, exothermic)

$rate = k[A][B]$

9. Draw an energy level diagram that represents the reaction given in Q8.



$K_e = \frac{[I]^2}{[A][B]}$

$rate = k[I]^2$

$= \underbrace{k K}_{k_{obs}} [A][B]$

Part II. (24 pts, 1 pt for each answer)

1. Which of the statements below about reaction rates are correct? Identify the correct statements by circling letters on the following list.

a b (c) (d) (e) (f) g h

a) Catalyzed and uncatalyzed reactions have the same rate laws, but different values of k.
b) In the presence of a catalyst, there are more collisions between reactant molecules.
c) A rate law could include the concentration of a catalyst.
d) At higher temperature a larger fraction of molecules have enough energy to get over the activation energy barrier.
e) The value of the rate constant k increases as the temperature increases.
f) The average kinetic energy of gaseous reactant molecules depends on temperature.
g) The rate of an endothermic reaction increases if the temperature is lowered.
h) The half-life of a first-order reaction depends on reactant concentration.

2. Which statements below about mechanisms are correct? Identify the correct statements by circling letters on the following list.

(a) b (c) d (e) f (g) h

a) It is possible to predict a rate law for a single step reaction.
b) In a multi-step reaction, only one step can be slow and rate determining.
c) A graph of ln k vs. 1/T will give a straight line.
d) It is possible to have an intermediate in a one-step reaction.
e) There must be at least one intermediate in a two-step reaction.
f) All single step reactions are first order in reactant concentration.
g) It is possible to predict a rate law of a multiple step reaction if the mechanism is known.
h) It is possible to prove a mechanism of a reaction by determining its rate law.

3. Which statements below about equilibrium are correct? Identify the correct statements by circling letters on the following list.

(a) b c (d) (e) f g (h)

a) All chemical reactions eventually reach equilibrium.
b) A large value of K indicates that the reaction will be reactant-favored.
c) Doubling the stoichiometric coefficients in the equilibrium equation changes the value of K by a factor of 2.
d) K_c and K_p for the equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ have the same values.
e) For an endothermic reaction, the value of K will increase if the temperature increases.
f) Following a volume increase (and pressure decrease), the $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ system will adjust by shifting to the left (more PCl_5 forms).
g) At equilibrium forward and reverse reactions cease to occur.
h) The value of an equilibrium constant doesn't change if a catalyst is added.

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Part III. (27 pts)

1. A vessel contains iodine (purple), H_2 and HI (both colorless) at equilibrium: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$. The purple color of the mixture fades as temperature is raised. Is the reaction forming HI exothermic or endothermic?

endothermic

2. The value of the equilibrium constant K for the reaction in in Q1 is 56. What is the value of K for the reaction $HI(g) \rightleftharpoons 1/2\ H_2(g) + 1/2\ I_2(g)$?

0.13

$K_2 = \frac{1}{\sqrt{56}}$

3. A flask contains: $[H_2] = 0.024$ mol/L, $[I_2] = 0.036$ mol/L, and $[HI] = 0.15$ mol/L. How will [HI] change to reach equilibrium (increase [HI] or decrease [HI])? ($K_c = 56$)

incr [HI]

$Q = \frac{[0.15]^2}{[0.024][0.036]} = 26$ smaller than 56;

4. For the equilibrium $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$: Into a 1.0 L flask, you put **A** moles of each of the three species. When equilibrium is attained the concentration of NH_3 is 1.4 A mol/L. What are the concentrations of N_2 and H_2? Fill the answer into the ICE table below.

	$[N_2]$ mol/L	$[H_2]$ mol/L	$[NH_3]$ mol/L
I	A mol/L	A mol/L	A mol/L
C	−0.2 A	−0.6 A	+0.4A
E	0.8A	0.4 A	1.4A mol/L

5. To maximize conversion of H_2 and N_2 to NH_3 at equilibrium, should pressure and temperature be high or low? (Formation of NH_3 is exothermic)

P high T low

6. For the reaction $3/2\ O_2(g) \rightleftharpoons 2\,O_3(g)$ $K = 2.5 \times 10^{-29}$. Is the reverse reaction, **decomposition of O_3 to form O_2** product- or reactant-favored?

product-favored

7. Write the equilibrium constant expression for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K = [CO_2]$

8. Solid $CaCO_3$ is heated at 600 °C to establish equilibrium, at which time the pressure of CO_2 is 22 mm Hg. The volume of the container is made smaller. When equilibrium is reattained, what is the pressure of CO_2? Assume the temperature does not change.

22 mm Hg

9. What happens to $[CO_2]$ if more $CaCO_3(s)$ is added to the equilibrium system in Q7? (increases, decreases. or doesn't change)

doesn't change

Part IV. (24 pts)

1. (12 pts) The thermal decomposition of nitrous oxide, $2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$ is first order in $[N_2O]$. At 967 K, $t_{1/2} = 6.3$ min. Assume that you start, initially, with 2.4 moles of N_2O in a 1.2 L vessel.

a) (10 pts) After 15 min. what fraction of N_2O will have decomposed?

$$\ln\left[\frac{A}{A_0}\right] = -kt = -\left(\frac{0.693}{6.3\,\text{min}}\right)(15\,\text{min})$$

$$\ln(f) = 0.19$$

↑ fraction remaining

so fraction remaining = 0.19

fraction decomp. = 0.81

Answer: 0.81

b) (2 pts) After 6.3 minutes, how many moles of O_2 have been formed?

In this time (one half-life) half of the N_2O has reacted. That is $\frac{1}{2} \times 2.4 = 1.2$ moles.

Decomp. of 1.2 mol N_2O forms 0.6 moles O_2

Answer: 0.60 moles O_2

2. For the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ at 545 K, the value for K = 7.6×10^{-6}. A 0.64 mol sample of $COCl_2$ is placed in a 2.0 L flask, and heated to 545 K.

a) (10 pts) Calculate the equilibrium concentrations of all species in the system at equilibrium. The ICE table is drawn below to help you do this calculation.

	$COCl_2(g)$	$CO(g)$	$Cl_2(g)$
I (amt)	0.64 mol		
I (conc)	0.32 m/L	0	0
C (conc)	$-x$	$+x$	$+x$
E (conc)	$0.32 - x$	x	x

$$K = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$7.6 \times 10^{-6} = \frac{(x)(x)}{(0.32 - x)}$$ assume small

$$\frac{x^2}{0.32} = 7.6 \times 10^{-6}$$

$$x = 0.0016$$

$[COCl_2]$ 0.32 m/L

$[CO]$ 1.6×10^{-3} m/L

$[Cl_2]$ 1.6×10^{-3} m/L

b) (2 pts) What percentage of $COCl_2$ has decomposed when equilibrium has been reached?

$$\% = \frac{1.6 \times 10^{-3} (100)}{0.32} = 0.50\ \%$$

Answer: 0.50 %