β

Name Key (Please Print)

Student Number______________

Chem 116 - Section 1
Hour Examination II
April 11, 2007

This test consists of seven (7) pages, including this cover page. Be sure your copy is complete before beginning your work. If this test packet is defective, ask for another one.

Useful Information

$R = 0.08206$ L·atm/K·mol = 8.314 J/K·mol K = °C + 273 $K_p = K_c(RT)^{\Delta n}$ $t_{1/2} = 0.693/k$

DO NOT WRITE BELOW THIS LINE

1.

2.

3.

4.

5.

TOTAL

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1. (20 points; 4 points each part) Circle the correct answer to each of the following.

a. Consider the reaction $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$, for which the rate is defined as $Rate = d[CCl_4]/dt$. At any time in the course of this reaction, the rate of disappearance of $Cl_2(g)$ is equal to

Rate   (4 × *Rate*)   ¼ × *Rate*   2 × *Rate*   ½ × *Rate*

b. The reaction $AB(g) \rightarrow A(g) + B(g)$ has the rate law $Rate = k[AB]$ and has a half-life of 12.0 s. If the initial concentration of AB is 1.00 mol/L, what will be the concentration of AB after 48.0 s?

0.000 mol/L   0.500 mol/L   0.250 mol/L   0.125 mol/L   (0.0625 mol/L)

c. For the reaction described in part b, what is the value of the rate constant, k, with the appropriate units?

0.125 L/mol/s   ($0.0578\ s^{-1}$) $0.0833\ s^{-1}$ 1.00 L/mol/s $4.00\ s^{-1}$

d. For the reaction in part b, data were collected to follow concentration of AB(g) with elapsed time. Which of the following plots of these data would yield the indicated information?

A plot of [AB] vs. time would give a straight line whose slope is k.

A plot of 1/[AB] vs. time would give a straight line whose slope is k.

A plot of ln [AB] vs. time would give a straight line whose slope is k

(A plot of ln [AB] vs. time would give a straight line whose slope is $-k$)

A plot of ln [AB] vs. time should give straight line with a slope equal to $-E_a/R$.

e. For the reaction described in part b, if rate constants, k, were determined at various absolute temperatures, T, a plot of ln k vs. $1/T$ would give a straight line whose slope is

$-E_a$ $-E_a/RT$ ($-E_a/R$) $\ln A$ $t_{1/2}$

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2. (16 points) Consider the reaction equilibrium

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

for which $\Delta H^{\circ} = -196.6$ kJ/mol in the forward direction.

a. (4 points) An empty vessel is charged with $SO_3(g)$ to a pressure of 0.573 atm. When equilibrium is established at 900 K, the partial pressure of $O_2(g)$ is 0.224 atm. Fill in the following table with the missing information. [Caution: Pay attention to the reaction stoichiometry!]

	$SO_2(g)$	$O_2(g)$	$SO_3(g)$
Initial (atm)	0	0	0.573
Change (atm)	+0.448	+0.224	−0.448
Equilibrium (atm)	0.448	0.224	0.125

b. (6 points) In the space below, write the expression for the equilibrium constant K_p for the reaction, and calculate its numerical value.

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2\ P_{O_2}} = \frac{(0.125)^2}{(0.448)^2(0.224)} = 0.347_5 = 0.348\ \text{atm}$$

c. (3 points) If the total pressure on the system at equilibrium were increased, would the reaction form more products, more reactant, or stay the same?

Answer more product

d. (3 points) If the temperature were increased, would the new equilibrium mixture contain more products, more reactant, or stay the same?

Answer more reactants

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3. (24 points) Consider the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

for which $K = 47.9$ at 458 °C. A one-liter vessel at 458 °C is filled with 0.300 mol $H_2(g)$, 0.300 mol $I_2(g)$, and 0.600 mol HI(g).

a. (4 points) Will the reaction proceed to the right or to the left to achieve equilibrium?

$Q = \frac{(0.600)^2}{(0.300)^2} = 4 << K_c$ Answer right

b. (20 points) Calculate the concentrations $[H_2]$, $[I_2]$, and [HI] for the system when equilibrium is established at 458 °C. (Show work in the space provided.) [Note: This calculation *does not* require solving a quadratic equation.]

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$0.300 - x \quad 0.300 - x \quad 0.600 + 2x$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.600+2x)^2}{(0.300-x)^2} = 47.9$$

$$\frac{0.600+2x}{0.300-x} = 6.92$$

$$0.600 + 2x = 2.07_6 - 6.92x$$

$$8.92x = 1.47_6$$

$$x = 1.47_6 / 8.92 = 0.165_5 = 0.166 \text{ mol/L}$$

$$[H_2] = [I_2] = 0.300 - 0.166 = 0.134 \text{ mol/L}$$

$$[HI] = 0.600 + (2)(0.166) = 0.932 \text{ mol/L}$$

Check: $Q = \frac{(0.932)^2}{(0.134)^2} = 48.3 \approx K_c \Rightarrow OK$

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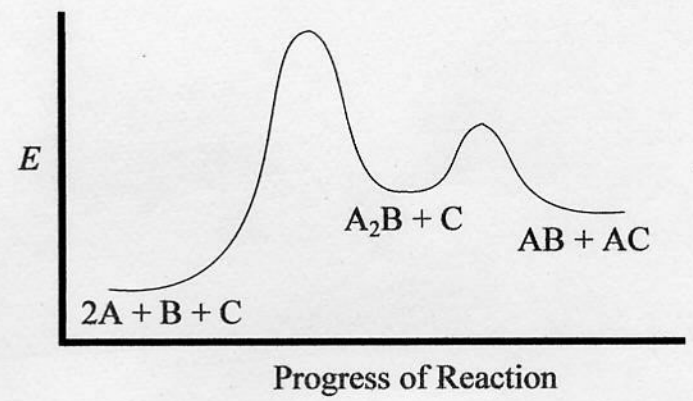
4. (20 points) The reaction $2\,A(g) + B(g) + C(g) \rightarrow AB(g) + AC(g)$ is thought to proceed by the following mechanism:

Step 1: $2\,A(g) + B(g) \xrightarrow{k_1} A_2B(g)$

Step 2: $A_2B(g) + C(g) \xrightarrow{k_2} AB(g) + AC(g)$

The reaction coordinate diagram for this mechanism is shown below.



a. (4 points) Identify any reaction intermediate species. A_2B

b. (8 points) Write the rate law expression for each step.

$rate_1 = k_1[A]^2[B]$ $rate_2 = k_2[A_2B][C]$

c. (4 points) Looking at the reaction coordinate diagram and deciding from it which step is rate determining, write the rate law that should be observed experimentally if this proposed mechanism is correct.

$Rate = k[A]^2[B]$

d. (4 points) Is the overall reaction exothermic or endothermic? endothermic

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5. (20 points) All parts of this question and the bonus question on the next page refer to the hypothetical reaction

$$X_2 + 2Y + Z \rightarrow XY_2 + XZ$$

a. (15 points) The following data were collected for the rate of the reaction.

Exp.	$[X_2]$ (M)	[Y] (M)	[Z] (M)	Initial Rate (M/s)
1	0.100	0.150	0.120	1.20×10^{-2}
2	0.400	0.150	0.120	2.40×10^{-2}
3	0.100	0.300	0.120	4.80×10^{-2}
4	0.100	0.150	0.360	1.20×10^{-2}

$\Rightarrow \text{Rate} \propto [X_2]^{1/2}$

$\Rightarrow \text{Rate} \propto [Y]^2$

$\Rightarrow \text{Rate} \propto [Z]^0$

What is the rate law for the reaction? *Rate* = *k* $[X_2]^{1/2}[Y]^2$

b. (5 points) What is the value of the rate constant, *k*, *with the appropriate units*, based on the data from Experiment #1? (Show work in the space below)

$$k = \frac{\text{Rate}}{[X_2]^{1/2}[Y]^2} = \frac{1.20 \times 10^{-2}\ M \cdot s^{-1}}{(0.100 M)^{1/2}(0.150 M)^2}$$

$$= 1.69\ M^{-3/2} \cdot s^{-1}$$

☞ See next page for bonus question related to this question. ☜

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BONUS (5 points) The following mechanism has been proposed for this reaction.

$$X_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X \qquad \text{fast}$$

$$X + 2Y \xrightarrow{k_2} XY_2 \qquad \text{slow}$$

$$X + Z \xrightarrow{k_3} XZ \qquad \text{fast}$$

Prove that this mechanism has a rate law consistent with the correct observed rate law in part a.

$$\text{Rate} = \text{rate}_2 = k_2[X][Y]^2$$

$$k_1[X_2] = k_{-1}[X]^2 \Rightarrow [X]^2 = \left(\frac{k_1}{k_{-1}}\right)[X_2]$$

$$[X] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[X_2]^{1/2}$$

$$\text{Rate} = \text{rate}_2 = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[X_2]^{1/2}[Y]^2$$

$$= k[X_2]^{1/2}[Y]^2$$