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Name Key (Please Print)

Student Number________________________

Chem 104 - Section 1
Hour Examination II
April 5, 2006

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 $CH_4(g) + 2H_2S(g) \rightarrow CS_2(g) + 4H_2(g)$, for which the rate is defined as $Rate = d[CS_2]/dt$. At any time in the course of this reaction, the rate of disappearance of $H_2S(g)$ 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 16.0 s. If the initial concentration of AB is 1.00 mol/L, what will be the concentration of AB after 24.0 s?

0.000 mol/L   0.177 mol/L   0.354 mol/L   0.630 mol/L   0.667 mol/L

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

0.0289 L/mol/s   0.0433 s^{-1} 0.0722 s^{-1} 1.00 L/mol/s   1.50 s^{-1}

d. Kinetic data are collected for the reaction described in part b at several temperatures, and a value of *k* is determined at each temperature. Which of the following plots of these data would yield the indicated information?

A plot of k vs. T should be a straight line with a slope equal to E_a.

A plot of $\ln k$ vs. $1/T$ should be a straight line with a slope equal to E_a/R.

A plot of $\ln k$ vs. $1/T$ should be a straight line with a slope equal to $-E_a/R$.

A plot of k vs. $1/T$ should be a straight line with a slope equal to $-E_a/R$.

A plot of $1/k$ vs. T should be a straight line with a slope equal to E_a/R.

e. For the reaction described in part b, at any temperature a plot of ln [AB] vs. *t* (time) should give a straight line whose slope is

E_a $\ln [AB]_o$ $-k$ $t_{1/2}$ $\ln A$

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2. (16 points) Consider the reaction equilibrium

$$3NO(g) \rightleftharpoons NO_2(g) + N_2O(g)$$

for which $\Delta H^{\circ} = -155.7$ kJ/mol in the forward direction.

a. (4 points) An empty one-liter vessel is charged with 0.882 mol NO(*g*). When equilibrium is established at 300 K it contains 0.186 mol of $N_2O(g)$. Fill in the following table with the missing information.

	$3NO(g)$ $\rightleftharpoons$	$NO_2(g)$ +	$N_2O(g)$
Initial (mol/L)	0.882	0	0
Change (mol/L)	−0.558	+0.186	+0.186
Equilibrium (mol/L)	0.324	0.186	0.186

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

$$K_c = \frac{[NO_2][N_2O]}{[NO]^3} = \frac{(0.186)(0.186)}{(0.324)^3} = 1.02$$

c. (3 points) If additional NO(*g*) were added to the equilibrium mixture, would the reaction form more products, more reactant, or stay the same?

Answer more products

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

Answer more products

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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 found to contain 0.600 mol $H_2(g)$, 0.600 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?

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.]

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K = 47.9$$

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

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

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

$$4.15_2 - 6.92x = 0.600 + 2x$$

$$8.92x = 3.55_2$$

$$x = 0.398$$

$[H_2] = [I_2] = 0.600 - 0.398 = 0.202$ mol/L

$[HI] = 0.600 + (2)(0.398) = 1.40$ mol/L

Check:

$$Q = \frac{(1.39_6)^2}{(0.202)^2} = 47.7 \Rightarrow \text{OK}$$

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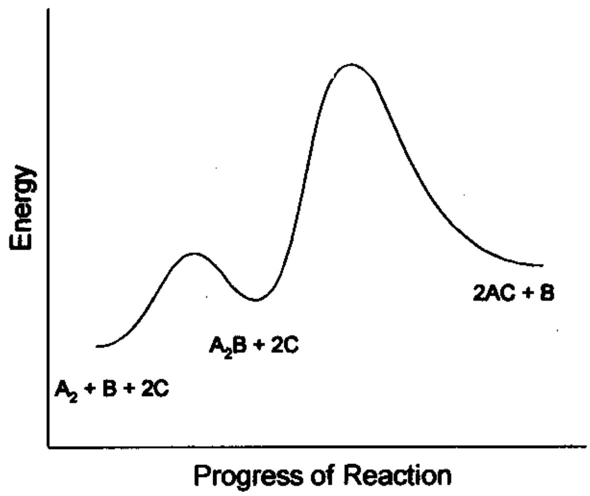
4. (20 points) The catalyzed reaction $A_2(g) + 2C(g) \rightarrow 2AC(g)$ is thought to proceed by the following mechanism:

Step 1: $A_2(g) + B(g) \xrightarrow{k_1} A_2B(g)$

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

The reaction profile for this two-step mechanism is shown below.



a. (3 points) Identify any reaction intermediate species. A_2B

b. (3 points) Identify the catalyst species. B

c. (4 points) Which step (Step 1 or Step 2) is rate determining? Step 2

d. (4 points) Write the rate law expression for each step.

$rate_1 = k_1[A_2][B]$ $rate_2 = k_2[A_2B][C]^2$

e. (4 points) Is the proposed mechanism plausible if the observed rate is $Rate = k[A_2][B]$?
no

f. (2 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

$$X_2 + Y + Z \rightarrow XY + XZ$$

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	0.160	0.140	1.20×10^{-2}	
2	0.400	0.160	0.140	2.40×10^{-2}	$\Rightarrow Rate \propto [X_2]^{1/2}$
3	0.100	0.640	0.140	4.80×10^{-2}	$\Rightarrow Rate \propto [Y]$
4	0.100	0.160	0.420	3.60×10^{-2}	$\Rightarrow Rate \propto [Z]$

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

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)

$$k = \frac{1.20 \times 10^{-2}\ M/s}{(0.100M)^{1/2}(0.160M)(0.140M)} = 1.69\ M^{-3/2}\ s^{-1}$$

☞ 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.

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

$$X + Y + Z \xrightarrow{k_2} XYZ \qquad \text{slow}$$

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

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

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

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

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