Name _____ Slayter Box _____

Hour Examination 3 February 27, 2003

General Chemistry (CHEM 122-01)

Kinetics & Equilibrium

Dr. Bennett

QUESTIONS 1, 2 and 3 each have many parts, but are not calculation based.
QUESTIONS 4 and 5 have calculation parts.

PLEASE THINK about how to budget your time!!!

Please do not open until instructed

Kinetics & Equilibrium

Notes:

* This exam consists of **5 questions on 7 pages** (including this cover page). Please check to make sure that you have a complete copy of the exam.
** Please do not simply give me answers. Give me well-supported answers. Numerical answers that are not backed by supporting calculations will receive minimal credit.*
* Please write clearly; if I can't read your answer, I can't give you credit for your answer.
* Please note that different questions are worth different numbers of points. Plan your time accordingly.
* Remember to include units and significant figures where appropriate.
* No books or notes are to be used on this exam.
* Please do NOT share calculators; if you need a calculator but do not have one, please let me know!

** If you feel that you would be better able to answer **any** question if you had additional information, please do not hesitate to ask for it.* I will happily provide any information that I feel will help you answer the question without compromising the efficacy and fairness of the test.

Question	Possible	Score
1	21	
2	12	
3	12	
4	12	
5	13	
TOTAL	70	
percent:		

The Quadratic Equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Some equations you *might* use:

$S = k_H \times P$

Arrhenius equation: **$k = Ae^{-Ea/RT}$**

$P_A = P_A° \times X_A$

$\Delta T_b = i\, K_b \times m$

Integrated rate laws:

zero-order **$[A]_t = -kt + [A]_o$**

$\Delta T_f = i\, K_f \times m$

first-order **$ln\,[A]_t = -kt + ln\,[A]_o$**

second-order **$1/[A]_t = kt + 1/[A]_o$**

1. For each of the following situations, please answer the question in one or a few words, or indicate that there is INSUFFICIENT INFORMATION for you to be sure of the answer. Although you need not do so for full credit, if you would like to ensure that I understand the reasoning behind your answer, you may justify your choice in one short sentence.

a) One of the reactions that we discussed in class was

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

This reaction is second order with respect to NO_2. If two experiments are performed in which the [CO] is kept constant, but the [NO_2] is three times as high in experiment #2 as in experiment #1, how much faster would you expect the rate of reaction to be in experiment #2?

b) Consider the decomposition of dinitrogen pentoxide gas:

$$N_2O_{5(g)} \rightarrow 2\ NO_{2(g)} + 1/2\ O_{2(g)}$$

An experiment is performed in which it is found that nitrogen dioxide is formed at a rate of 3.6 M/sec. What would you predict to be the rate of formation of molecular oxygen in this experiment?

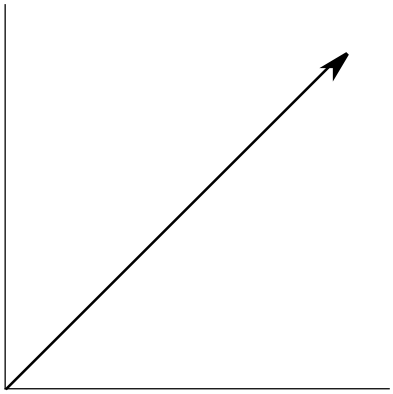
c) Consider two reactions occurring at a certain temperature. In reaction A, the products of the reaction are more stable than the reactants; in reaction B, the reactants are more stable. Which reaction will be faster?

d) Consider two reactions occurring at a certain temperature. For reaction A, the activation energy is 85 kJ/mol; for reaction B, it is 65 kJ/mol. Which reaction will be faster?

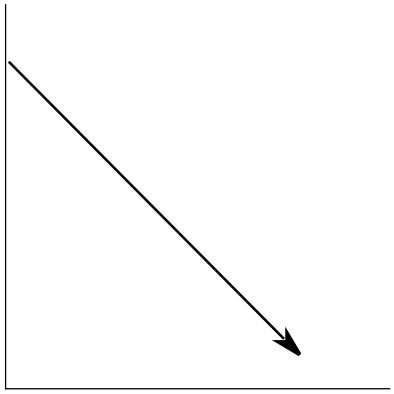
e) True or false: Increasing the temperature of a reaction AND increasing the concentration of one of the reactants BOTH increase the rate constant for the reaction.

Question 1 continued with OTHER SHORTER ANSWER QUESTIONS.

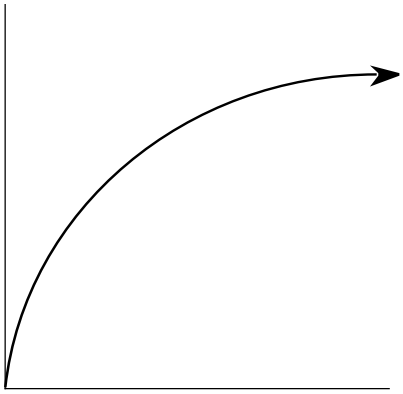
(f) Which of the following graphs best depicts how the rate of a reaction changes when the temperature is changed (everything else kept the same)? **CIRCLE YOUR CHOICE**



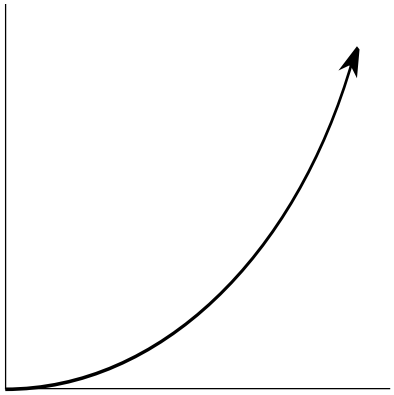
Temperature



Temperature



Temperature



Temperature

(g) Proponents of collision theory explain the temperature dependence of reaction rates by considering the rate constant k to be the product of three factors:

$$\mathbf{k = Zfp}$$

For example, f is the fraction of molecular collisions that occur with enough energy to get over the activation energy barrier from reactants to products ($f = e^{-Ea/RT}$).
In **one sentence each**, give a definition of the terms Z and p.

2. Given the following reaction, ***circle*** the direction of the equilibrium shift (towards products, towards reactants, or no change) when the following changes to the system are made:

$$2\ H_{2(g)} + C_{(s,\ graphite)} \Leftrightarrow CH_{4(g)} \qquad \Delta H° = -74.85\ kJ \text{ (exothermic)}$$

(a) Adding solid carbon graphite.

towards products towards reactants no change

(b) Cooling the system.

towards products towards reactants no change

(c) Increasing the partial pressure of hydrogen gas.

towards products towards reactants no change

(d) Increasing the total pressure by decreasing the volume.

towards products towards reactants no change

(e) Adding a catalyst to the system.

towards products towards reactants no change

(f) Which of these changes would change the value of the equilibrium constant? *Circle letter(s)*

(a) (b) (c) (d) (e)

3. Considering the energy profile shown below for the reaction:

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$$

please answer the following questions:

(a) Which of the labeled points (A~F) represents the energy of the transition state for the rate determining step? _____

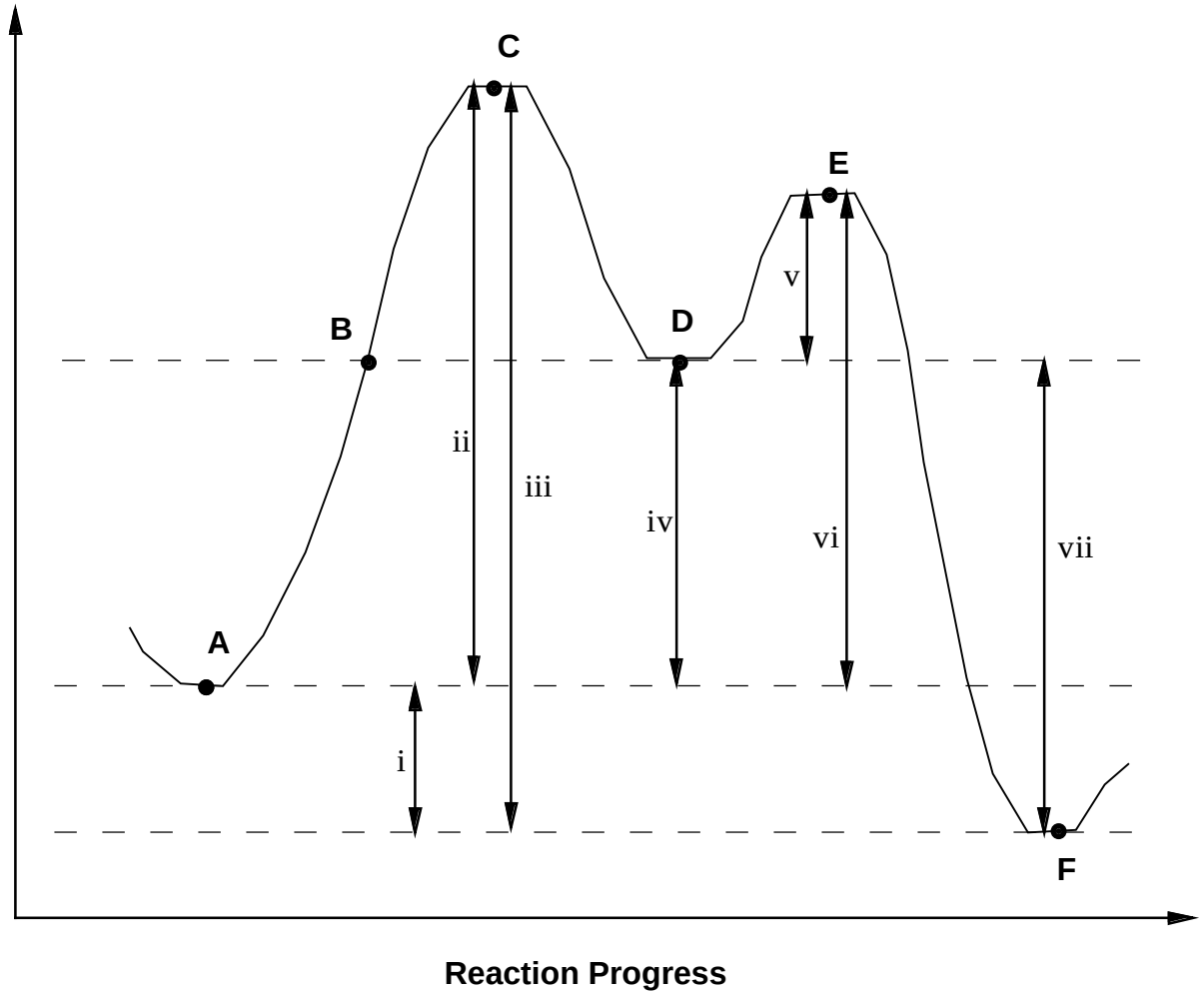
(b) Is the molecular species present at point D or point E going to be more stable? _____

(c) which of the **numbered** energy differences represents the energy change of the overall reaction?_____

(d) which of the **numbered** energy differences represents the activation energy for the ***forward*** reaction?_____

(e) which of the **numbered** energy differences represents the activation energy for the ***reverse*** reaction?_____

(f) An enzyme called carbonic anhydrase catalyses this reaction. Draw on the diagram a possible energy profile for the reaction run under catalyzed conditions.

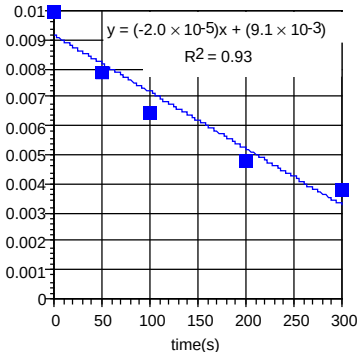


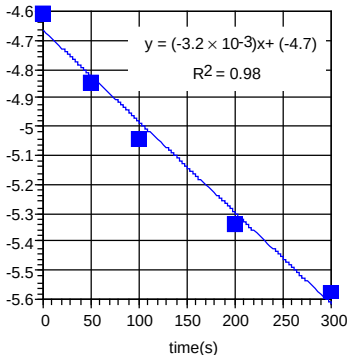
4. The decomposition of $NO_2(g)$ at 300 °C was studied by measuring $NO_2(g)$ concentration versus time. The following data were obtained for the reaction:

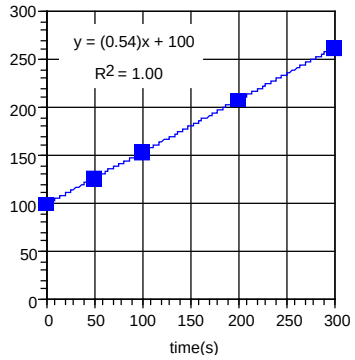
$$NO_2(g) \rightarrow NO_{(g)} + {}^1/_2\, O_2(g)$$

time (s)	**[NO_2] (M)**
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

To determine the order of the reaction you make the following plots: [NO_2] vs. t, ln[NO_2] vs. t, and 1/[NO_2] vs. t. For each graph you ask the computer to do a least squares linear fit to the data. The graphs and equations are shown below.







(a) Based on your interpretation of these graphs, is the reaction zero, first, or second order? ***Why?***

(b) Write the rate law for the reaction (not the integrated rate law).

(c) Determine the value of the rate constant k (be sure to use the proper units).

(d) In the lab next door, they are also studying the decomposition of $NO_{2(g)}$ at 300 °C. They prepare a vessel with 0.0350 M NO_2 and begin the reaction. How long will it take for the concentration of $NO_{2(g)}$ in their vessel to drop to 0.0016 M?

5. A mixture that initially contains 0.500 mol $SbCl_3$, 0.175 mol Cl_2, and 4.250 mol $SbCl_5$ comes to equilibrium in a 5.00 L reaction vessel at 648 °C. The reaction is:

$$SbCl_{3(g)} + Cl_{2(g)} \Leftrightarrow SbCl_{5(g)}$$

with $K_c = 40.0$.

(a) Determine the direction the reaction moves to attain equilibrium.

(b) Calculate the equilibrium concentration of each gas.