Exam Two **CHM 205 (Dr. Mattson)** **7 February 2005**	***Academic Integrity Pledge:*** *In keeping with Creighton University's ideals and with the Academic Integrity Code adopted by the College of Arts and Sciences, I pledge that this work is my own and that I have neither given nor received inappropriate assistance in preparing it.* *Signature:*

Instructions: Show all work whenever a calculation is required! You will receive credit for how you worked each problem as well as for the correct answer. This exam is worth 50 points. BOX YOUR ANSWERS!

1. (2 pts) Write the equilibrium expression, K_c, for:

(a) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\ H_2(g)$

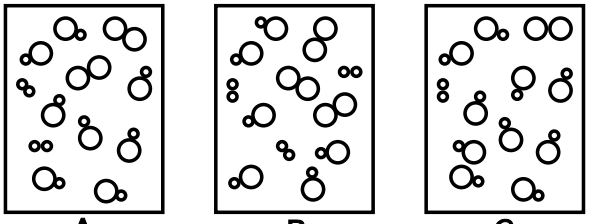
2. (2 pts) Write the equilibrium expression, K_p, for:

(b) $NH_4NO_3(s) \rightleftharpoons N_2O(g) + 2\ H_2O(g)$

3. (3 pts) Consider the reaction for which $K_c = 16$:

$$A_2 + B_2 \rightleftharpoons 2\ AB \quad K_c = 16$$

(a) Which of the pictures below represents a system at equilibrium? (A is represented by the small circles and B is the large circles.) Complete the checklist that appears below the figure.



Flask A	Flask B	Flask C
[ ] Already at equilibrium	[ ] Already at equilibrium	[ ] Already at equilibrium
[ ] Must shift L	[ ] Must shift L	[ ] Must shift L
[ ] Must shift R	[ ] Must shift R	[ ] Must shift R

4. (3 points) Match these equilibrium arrows with the most reasonable equilibrium constant. For each, circle "A," "B," or "C."

A B C Q ⟺ W (A) $K = 2.5 \times 10^{-6}$

A B C R ⟺ Y (B) $K = 9.8 \times 10^{-1}$

A B C S ⟺ Z (C) $K = 7.7 \times 10^{3}$

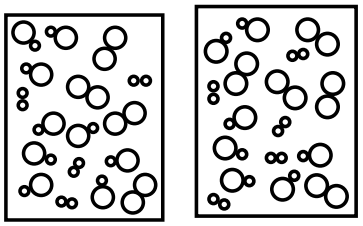
5. (4 pts) Suppose the following equilibrium is established by starting with 3.00 mole of $N_2H_4(g)$ in an evacuated 10.00-L container. Suppose further that when equilibrium is established, $[N_2] = 0.072$ M. Calculate K_c.

$$2\ N_2H_4(g) \rightleftharpoons N_2(g) + 2\ H_2(g)$$

6. (3 pts) The left figure below represents the following system at equilibrium at 900 K. The right figure represents the same equilibrium at 1000 K.

$$2\ HF(g) \rightleftharpoons F_2(g) + H_2(g) \quad \Delta H = ?$$

Determine if the forward reaction is endothermic or exothermic and *explain* your reason.



7. (3 pts) Consider the equilibrium below. If Br_2, I_2 and BrI were placed in a 5.00 L flask with initial concentrations of $[Br_2] = 3.00$ M, $[I_2] = 3.00$ M, and $[BrI] = 10.0$ M. (a) Determine if the system is at equilibrium. If not, which direction must it shift in order to attain equilibrium?

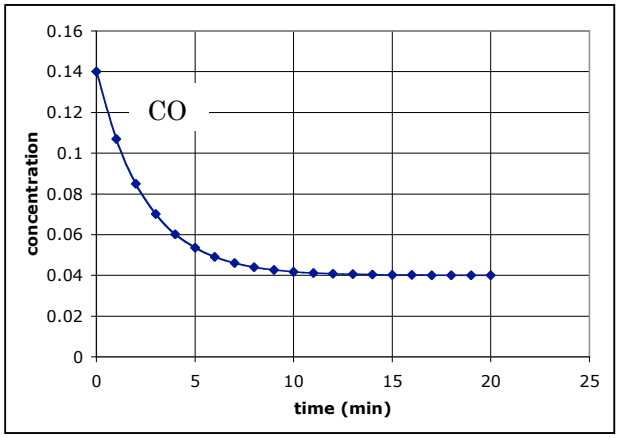
$$Br_2(g) + I_2(g) \rightleftharpoons 2\ BrI(g) \quad K_c = 7.9$$

(b) (4 pts) Calculate the equilibrium concentrations of all gases.

8. The rest of the exam consists of this multi-part question combining concepts from both the kinetics and equilibrium chapters. The graph and equilibrium below are used to answer all remaining questions. The graph displays the concentration of CO(g) as a function of time for the reaction given below. Initial concentrations: $[NO_2]$ = 0.10 mol/L; [CO] = 0.14 mol/L; $[CO_2] = [N_2]$ = 0.00 mol/L.

$$4\ CO(g) + 2\ NO_2(g) \rightleftharpoons 4\ CO_2(g) + N_2(g)$$

$$\Delta H = -1198\ kJ$$



8a (2 pts) On the graph above, identify the *kinetics region* and the *equilibrium region*.

8b (7 pts) Given the reaction stoichiometry, the initial concentrations given above and information from the graph, complete the ICE table below and than plot the concentrations of the other three gases on the graph: Sketch the lines for $[NO_2]$, $[CO_2]$ and $[N_2]$ starting at t = 0 s and ending at t = 20 min. Label each line! *Hint: Start by drawing the equilibrium concentrations for all four gases and then connect them to their initial (t = 0 s) concentration values with a line that shows approximate concentrations.*

	$CO_{(g)}$	$NO_{2(g)}$	$CO_{2(g)}$	$N_{2(g)}$
I				
C				
E				

8c (3 pts) What is the equilibrium constant, K_c in terms of concentrations of gases and what is the numerical value of K_c?

8d (3 pts) Suppose it was known that the reaction followed 2nd order kinetics in $NO_2(g)$. Which of the following mechanisms is consistent with the experimentally determined order?

Mechanism A:

Step 1. $NO_2 + NO_2 \rightarrow NO + NO_3$ Slow

Step 2. $CO + NO_3 \rightarrow CO_2 + NO_2$ Fast

Step 3. $NO + NO_2 \rightarrow N_2O_3$ Fast

Step 4. $N_2O_3 + CO \rightarrow CO_2 + N_2O_2$ Fast

Step 5. $N_2O_2 + CO \rightarrow CO_2 + N_2O$ Fast

Step 6. $N_2O + CO \rightarrow CO_2 + N_2$ Fast

Mechanism B:

Step 1. $NO_2 + CO \rightarrow NO + CO_2$ Slow

Step 2. $NO + NO_2 \rightarrow N_2O_3$ Fast

Step 3. $N_2O_3 + CO \rightarrow CO_2 + N_2O_2$ Fast

Step 4. $N_2O_2 + CO \rightarrow CO_2 + N_2O$ Fast

Step 5. $N_2O + CO \rightarrow CO_2 + N_2$ Fast

Explain your answer

8e (8 pts) Predict the effect that each of the following will have on the rate constant and the equilibrium constant. Write "I" for "increase," "D" for "decrease," and "NC" for "no change"

	rate	k_{rate}	K_c
increasing T			
adding a catalyst			
adding NO_2			
Decreasing the size of the container.			

8f (3 pts) Suppose at t = 20 min, additional CO were added so that the concentration instantaneously jumped to 0.06 mol/L. Plot the resulting concentrations *qualitatively* (showing them increasing or decreasing by "some" amount) for all four gases on the graph for the time period t = 20 min to t = 25 min.

9. (BONUS 1 point) Print your name here:

(For DocM's use)

Your exam score (50 possible): _____

Bonus pts: Max: _____ Earned: _____

Total Score (50 maximum) _____

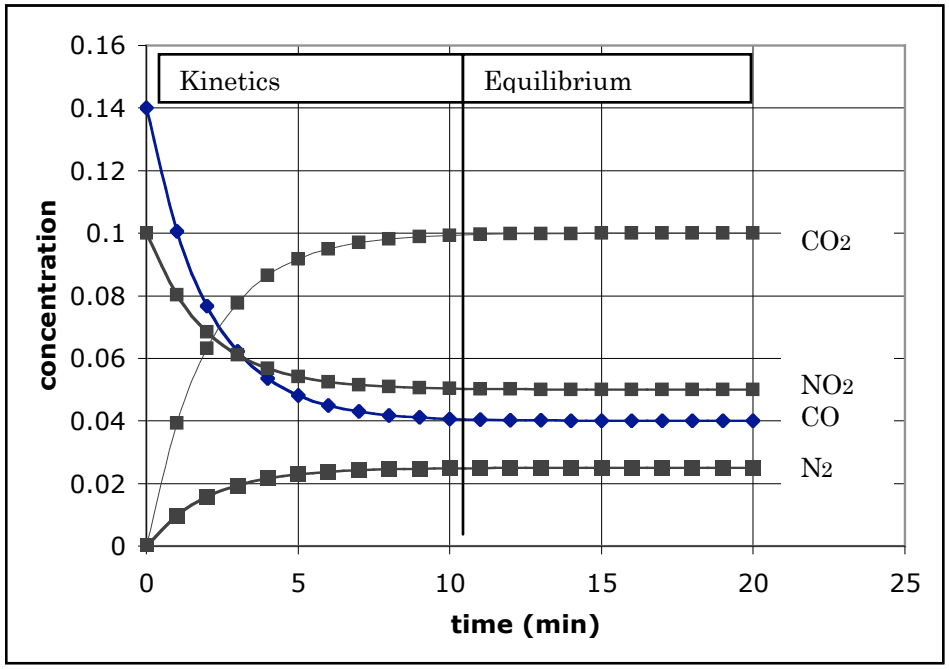
Determine your grade:
A ≥ 46.5; B+ ≥ 43.5; B ≥ 41.0;
C+ ≥ 37.5; C ≥ 34.00; D ≥ 30.00

Answers

1. $K_c = [H_2]^3[CO]/[CH_4][H_2O]$
2. $K_p = P_{N2O} \times P_{H2O}$
3. A is already at equilibrium; B must shift right and C must shift left
4. B, C, A
5. $K_c = 6.1 \times 10^{-2}$
6. endothermic
7. (a) Qc = 11, therefore must shift left

(b) [BrI] = 9.35 M; $[I_2] = [Br_2] = 3.33$ M

8. (a)



8b. Use the graph to solve for the equilibrium concentration of CO and then solve for x:

	$CO_{(g)}$	$NO_{2(g)}$	$CO_{2(g)}$	$N_{2(g)}$
I	0.14	0.10	0	0
C	-4x	-2x	+4x	+x
E	0.14-4x = 0.04 (from graph)	0.10-2x =0,05	0+4x = 0.10	0 + x = 0.025

8c. $K_c = 391$

8d. Mechanism A is the only one consistent with a rate that is second order in NO_2.

8e.

	rate	k_{rate}	K_c
increasing T	I	I	D
adding a catalyst	I	See note	NC
adding NO_2	I	NC	NC
Decreasing the size of the container.	I	NC	

Note: Adding a catalyst changes the mechanism so it isn't technically correct to say that the rate constant increases. The new rate constant is larger than the old one, however. I accepted wither NC or I. (Some people put NC, based on the principle that only a change in temperature can change the rate constant.

8f. I looked for CO spiking upward to 0.6 at t = 20 minutes. From 20 to 25, Lechatelier predicts that CO (the new concentration) and NO2 will decrease by 4x and 2x while CO2 and N2 will increase by 4x and 1x. The "x" thgis time is not the same as the previous x, however.