Chemistry 271 – 23XX **Your Name:** ______________________

Prof. Jason Kahn

University of Maryland, College Park **Your SID #:** ______________________

General Chemistry and Energetics

Exam I (100 points) **Your Section # or time:** ______________________

February 29, 2016

You have 53 minutes for this exam.

Explanations should be concise and clear. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$ $pH = -\log([H^+])$ $K_b = [HA][HO^-]/[A^-]$

$R = 0.08206$ L·atm/mole K $k_B = 1.38 \times 10^{-23}$ J/K $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$

$°C = °K - 273.15$ $P(v)dv = Cv^2 \exp(-mv^2/2kT)$ $\ln k = (-E_a/RT) + \ln A$

Integrated rate laws for 0, 1, 2 order:

$[A] = [A]_0 - kt$ $\ln[A] = \ln[A]_0 - kt$ $1/[A] = 1/[A]_0 + 2kt$

$t_{1/2} = [A]_0/(2k)$ $t_{1/2} = \ln 2/k$ $t_{1/2} = 1/(2k[A]_0)$

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. Explanations (21 pts)

(a; 9 pts) Briefly and generally describe the overall flow for using kinetic measurements to evaluate a proposed mechanism for a chemical reaction.

(b; 12 pts) Explain how the Maxwell-Boltzmann distribution of gas speeds leads to the Arrhenius equation for the temperature dependence of the rate constant. Sketch an Arrhenius plot with the axes, slope, and intercept labeled.

Score for the page____________

2. Ideal Gas Law (20 pts)

(a; 10 pts) A standard Size 300 gas cylinder has an internal volume of 49 L. In such a cylinder filled with nitrogen, treating the N_2 as an ideal gas, how many moles of N_2 are there and how much does the N_2 (MW 28) weigh, at a partial pressure of N_2 of 180 atm, at 21 °C?

(b; 3 pts) What volume would the contents of the cylinder occupy at 1 atm pressure?

(c; 2 pts) If one had the same cylinder filled with Argon (MW 40) at the same pressure and temperature, how many moles of Ar would it contain?

(d; 5 pts) Would the Ar atoms move on average faster or slower than the N_2 molecules, and why?

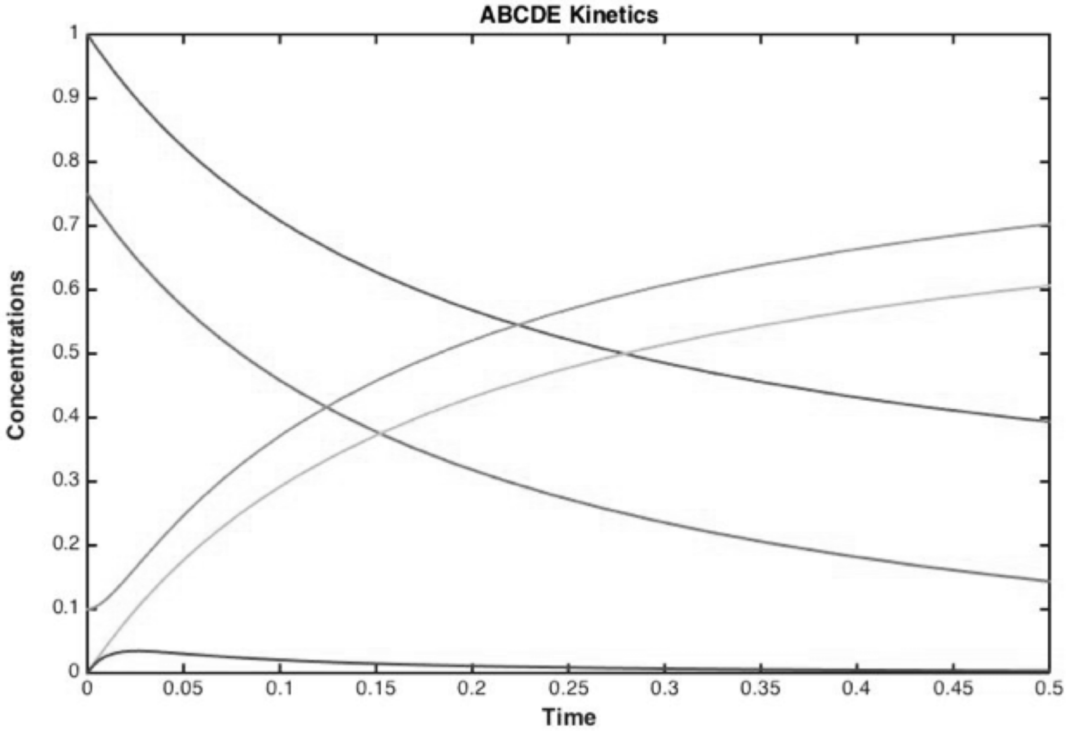
Score for the page____________

3. Kinetics (30 pts)

(a; 12 pts) The radioactive isotope ^{32}P has a half-life of 14.3 days, decaying into ^{32}S + e^-. The half-life is independent of the amount of ^{32}P. Write down the rate law for the decay process, and calculate the rate constant. What fraction of the initial sample remains after 6 months (182 days)?

The graph below shows kinetics for the reaction scheme below, where the reactions shown are elementary. We start with mostly A and B, with a smaller amount of C or E also present.

$$A + B \rightleftharpoons C + D$$
$$D \rightarrow E$$



Score for the page____________

(b; 5 pts) Label the five kinetic traces as (A or B), (A or B), C, D, and E. (There is no way to distinguish A and B from the information given.)

(c; 4 pts) Explain how you identified the curve that starts at Concentration = 0.1 as either C or E; it is subtle.

(d; 7 pts) The curve for D represents a steady state intermediate. Write down the differential rate equation for the concentration of intermediate D. What does the SSA tell us about the numerical value of d[D]/dt?

(e; 2 pts)Has the reaction reached equilibrium at t = 0.5? Circle one: Yes No . Explain how you know.

Score for the page____________

4. LeChatelier's Principle (29 pts)

The equilibrium below is called the Water-Gas Shift Reaction (WGSR). It is important in industrial hydrogen production. The WGSR is performed at high enough temperature that all of the components are gases at all times, and we assume that all the gases behave as ideal gases.

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Consider a mixture of CO and water that has been allowed to come to equilibrium, under conditions chosen so that at equilibrium there are substantial partial pressures of all four gases.

(a; 2 pts) What do we know about the overall rates of the forward and reverse reactions at equilibrium?

Now, additional pure CO is added to the reaction vessel. LeChatelier's principle tells us about what happens next, qualitatively.
(b; 6 pts) Explain which way the equilibrium shifts, and why, according to LeChatelier.

(c; 3 pts) If someone's answer to (b) had something to do with a response to a change in the total pressure of the gas mixture, it was wrong. Why?

(d; 6 pts) Now give an explanation for the shift in the equilibrium you described in (b) based on the kinetics of the forward and reverse reactions, as an alternative to LeChatelier's principle.

Score for the page____________

(e; 2 pts) When the mixture re-equilibrates, the final partial pressure of CO will be (circle one): equal to, more than, or less than the partial pressure before the addition of CO.

(f; 7 pts) The WGSR can be catalyzed by a variety of metal complexes, with complicated and irrelevant mechanisms, and the uncatalyzed reaction is slow enough to be ignored. If we start a reaction with large partial pressures of CO and water, no H_2 or CO_2, and a very small amount of catalyst, what rate law would you expect to observe for the kinetics of CO oxidation? Sketch the one form of the graph for the partial pressure of CO (P_{CO}) vs. time (choosing from among P_{CO} vs. time, $\ln(P_{CO})$ vs. time, and $1/P_{CO}$ vs. time) that gives a linear form from which we could extract a rate constant.

(g; 3 pts) If we doubled the amount of CO, what would happen to the measured rate constant under these conditions? If we doubled the amount of catalyst, what would happen to the measured rate constant?

Page	Score
2	/21
3	/20
4	/12
5	/18
6	/17
7	/12
Total	**/100**

Score for the page____________