Name_____

Chemistry 4A
Fall 1995
Professor Mathies

Section_____

TA_____

FINAL EXAM

Begin by writing your name on all pages. **You must show all your work in the space provided.** At the start, spend your time on the problems that you know how to do. Then go back and work on the more difficult problems in the time remaining. The more challenging problems are where you have an *. Tables, constants, graph paper and some equations will be found in the supplemental handout.

Good Luck!!

Problem 1 _____ (21)
Problem 2 _____ (24)
Problem 3 _____ (10)
Problem 4 _____ (10)
Problem 5 _____ (10)
Problem 6 _____ (10)
Problem 7 _____ (25)
Problem 8 _____ (25)
Problem 9 _____ (25)
Problem 10 _____ (10)
Problem 11 _____ (10)
Problem 12 _____ (10)
Problem 13 _____ (10)
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Total _____ (200)

21 1. Answer the following short questions:

(a) The acid dissociation constant of hypochlorous acid HClO is 3.0×10^{-8}. Calculate the pH of a 0.01 M solution of this acid in water.

(b) Circle the strongest and underline the weakest oxidizing agent. The reduction potential tables in the appendix may be useful.

Co^{2+} MnO_4^- Cu^{2+} K^+

(c) Circle the most acidic solution and underline the most basic solution.

NH_4Cl (1 M) HCN (1 M) sodium acetate (1 M) NaCl (1 M)

(d) A radioactive sample initially produced 1×10^5 disintegrations per minute (dpm); 28 days later it produced only 0.25×10^5 dpm. What is the halflife of the radioactive material in this sample? (1 day = 1440 min)

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2. Indicate whether each of these statements is true or false. Briefly explain your answer if the statement is false.

a) A second order rate constant of ~ 10^{10} s^{-1} M^{-1} is generally considered to be diffusion limited. T F

b) The minimum useful work available from a process is bounded by the magnitude of ΔG. T F

c) For any real process the entropy of the Universe increases. T F

d) The energy of activation is negative for spontaneous processes. T F

e) ΔG can be negative even if ΔG^o is positive. T F

f) $\Delta \varepsilon^o$ is < 0 when ΔG^o is < 0. T F

g) The reaction with the lowest activation energy will be the most sensitive to an increase in temperature. T F

h) The half-time of a second-order kinetic process depends on the reciprocal of the initial concentration. T F

10 3. Laidler studied the temperature dependence of the chirping of crickets and found that it follows the Arrhenius expression very nicely (J. Chem. Edu. **49**, 343, 1972). At 25° C the chirping rate from one cage of crickets was 25 min^{-1}, while at 35° C the rate increased to 60 min^{-1}. Calculate the apparent activation energy and preexponential factors that describe this experiment.

10 4. You are given an aqueous solution that contains 1.5×10^{-3} M $AgNO_3$, 0.800 M $CuNO_3$ and 1.0 M $Pb(NO_3)_2$. A solution of sodium iodide is then slowly added to precipitate these ions as the insoluble iodides. Which species will precipitate first? Which will precipitate next? What will the concentration of iodide be in solution when a precipitate first forms? K_{sp} (AgI) = 1.5×10^{-16}, K_{sp} (CuI) = 5.1×10^{-12}, and K_{sp} (PbI_2) = 1.4×10^{-8}.

10 5. You are examining the reaction A + B → C in an aqueous solution. One proposed mechanism for this reaction is the following:

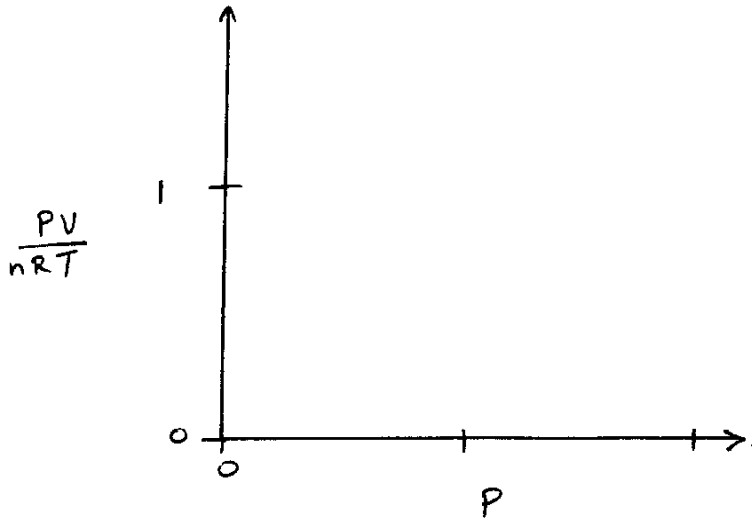
$A + OH^- \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} N^-$	fast and reversible
$N^- \xrightarrow{k_2} P^-$	slow
$P^- + B \xrightarrow{k_3} C + OH^-$	fast

(a) Is this mechanism consistent with the overall reaction? Why?

(b) What rate law is predicted by this mechanism?

(c) What additional experiments would you propose to test this mechanism?

10 6. The van der Waals equation is $\{P + an^2/V^2\}\{V - nb\} = nRT$. For CH_4 the van der Waals constants are: a = 2.25 atm L^2 mol^{-2} and b = 0.043 L mol^{-1}. Make a sketch of PV/nRT vs. P indicating the behavior of an ideal gas as well as that of CH_4. Which van der Waals correction term produces which deviation from the ideal gas behaviour? Explain the physical origin of each correction term.



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7. You are given stock solutions that are 1 M phosphoric acid H_3PO_4, 1 M monosodium phosphate NaH_2PO_4, and 1 M disodium phosphate Na_2HPO_4. Describe how you would make up 1 liter of a phosphate buffer solution having a pH of 7.0 and a total phosphate activity or concentration of 1×10^{-2} molar. The pH equilibria for phosphate that may be relevant for this problem are indicated below.

$$H_2O + H_3PO_4 \leftrightarrow H_2O^+ + H_2PO_4^- \qquad K_1 = 7.52 \times 10^{-3}$$

$$H_2O + H_2PO_4^- \leftrightarrow H_2O^+ + HPO_4^{2-} \qquad K_2 = 6.23 \times 10^{-8}$$

$$H_2O + HPO_4^{2-} \leftrightarrow H_2O^+ + PO_4^{3-} \qquad K_3 = 2.20 \times 10^{-13}$$

25 8. Consider a galvanic cell that is described by:

$$Ag \mid AgNO_3\,(0.001\ M) \parallel AuNO_3\ (0.5\ M) \mid Au\ (s)$$

(a) What are the reactions that occur at the anode, at the cathode, and the overall cell reaction. What is $\Delta\varepsilon^o$ for this cell at 25° C.

(b) Sketch and label the components of this cell indicating clearly the direction of electron flow, the direction of ion flow in the cell, and the location of the cathode and anode.

(c) What is ΔG^o for this cell reaction at 25° C?

(d) Calculate the cell voltage $\Delta\varepsilon$ under the given conditions at 25° C.

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9. In our laboratory studies of kinetics we exploited the idea that I_2 and I^- will rapidly form the complex ion I_3^- which can be easily detected as a colored starch complex. Let's explore the thermodynamics of this process.

$$I^- (aq) + I_2 (aq) \leftrightarrow I_3^- (aq)$$

(a) Use the appended tables to determine the value of ΔG° for this reaction.

(b) What is the equilibrium constant for this reaction at 25° C?

(c) Suppose you add enough iodine to a 1 molar NaI solution make the solution nominally 1×10^{-3} molar in I_2. After equilibrium is established what will the remaining concentration of I_2 be ?

(d) In order to increase the rate of I_3^- complex formation, you increase the temperature to 35° C. Will this increase or decrease the concentration of I_3^- that is eventually formed at equilibrium? Why? Quantitate your answer by calculating the equilibrium constant for this reaction at 35° C.

10 10. * Pyrazole has been proposed as a possible nontoxic inhibitor of LADH catalyzed oxidation of ethanol. The rate of oxidation of ethanol was measured for 4 micrograms LADH/mL with the following results:

[ethanol]	relative velocity	relative velocity (in presence of 1×10^{-5} M pyrazole)
8.0×10^{-3}	2.13	1.69
2.0×10^{-3}	1.82	1.03
1.0×10^{-3}	1.52	0.69
0.66×10^{-3}	1.35	0.52

Plot these data and determine the value of v_{max} and K_m in the absence and in the presence of the inhibitor. Based on your observations, propose a mechanism for how pyrazole inhibits this enzyme. Graph paper will be found in the appendix material.

10 11. If you put 100 bacteria into a 1 liter flask containing appropirate growth media at 40° C, they will grow and you will find the following results.

time (min)	number of bacteria
0	100
30	200
60	400
90	800
120	1600

(a) What is the order of the kinetics of this growth process?

(b) What is the rate constant for this reaction?

(c) How long would it take to get 10^6 bacteria?

10 12. In your kinetics lab on the oxidation of iodide by persulfate, you measured the rate constant of solutions at the temperature of the spectrophotometer compartment which you assumed to be the same as the ambient lab temperature. The overall reaction was $3I^- + S_2O_8^{2-} \rightarrow I_3^- + 2SO_4^{2-}$ where

$$\text{rate} = k[I^-]^m [S_2O_8^{2-}]^n$$

(a) Unfortunately, the temperature in the compartment was actually 25° C which is 2° C higher than the laboratory temperature. Does this make the reaction faster or slower? Why?

(b) Estimate the percentage increase (or decrease) in the rate that occurs. The activation energy for this reaction is 60 kJ/mole.

(c) The path length of the spectrophotometer cell is specified to be 1.00 ± 0.005 cm. If the actual path length was 1.01 cm while you used 1.00 in your calculations and analysis of the rate of this reaction, would your calculated k be larger or smaller than the "correct" one? What would be your percentage error?

10 13.* You have decided to work on an undergraduate research project to test the Third Law of Thermodynamics. Your project is to produce a crystal of CO and then to determine its entropy at as close to 0 K as your apparatus can go. (At UCB the apparatus is generally quite good!)

(a) Based on your knowledge of the Third Law, what do you expect to measure for the residual entropy of CO at 0 K and why?

(b) When you actually do the experiment, you find that your result depends on how you make the CO crystal. In particular, when you made the CO solid by rapidly blowing CO gas on the cryostat, the residual entropy at a temperature of ~0 K turns out to be close to the value Rln 2. Qualitatively explain why the residual entropy is elevated. Develop a model for the structure of the CO crystal and the molecular orientations therein that allows you to quantitatively understand (ie. predict) this result.