Name_____

Chemistry 4A
Fall 1996
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. Tables, constants, graph paper and some equations will be found in the supplemental handout.

Good Luck!!

Problem 1 _____ (20)

Problem 2 _____ (15)

Problem 3 _____ (10)

Problem 4 _____ (10)

Problem 5 _____ (15)

Problem 6 _____ (15)

Problem 7 _____ (20)

Problem 8 _____ (25)

Problem 9 _____ (25)

Problem 10 _____ (20)

Problem 11 _____ (10)

Problem 12 _____ (15)

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Total _____ (200)

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20

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

a) Raising the temperature will shift an equilibrium toward the products if ΔH^o is < 0. T F

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

c) The entropy of the Universe increases for all types of processes. T F

d) The boiling point of a solvent is always decreased by adding nonvolatile solutes. T F

e) The second order rate constant for the formation of H_2O from H^+ and OH^- is ~10^{11} $M^{-1}s^{-1}$ T F

f) Raoult's Law states that the vapor pressure over a solution depends on the mole fraction of the solvent. T F

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

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

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2. Answer the following short questions:

(a) On the east coast people often sprinkle solid NaCl or $CaCl_2$ on the streets to melt the ice. Assuming that you can buy NaCl and $CaCl_2$ for the same price per pound (or gram), which is the best reagent for melting the ice and why? The molal freezing point constant for water is 1.86 K/molal.

(b) A collection of cells having an internal salt concentration that is effectively 0.2 molar NaCl is dumped into a beaker of distilled water. The membranes of these cells are semipermeable to water. What happens and why? Calculate the osmotic pressure that could buildup in principle if the cell membrane was strong enough. T = 298 K.

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10 3. The age of a bottle of wine may be determined by measuring its radioactive tritium content. Natural tritium is present in a low steady state concentration in water vapor. It is formed primarily by cosmic ray irradiation of water vapor in the upper atmosphere, and it decays spontaneously by a first-order process with a half-life of 12.5 years. The formation reaction does not occur significantly once the wine is trapped in a glass bottle at the surface of the earth. Calculate the age of a vintage bottle of wine that is 20% as radioactive as a freshly bottled sample.

10 4. There is concern that synthetic bromine-containing compounds may contribute to the destruction of the ozone layer along with the long suspected chlorine-containing compounds. In this case BrO can enter into the overall reaction mechanism along with ClO as indicated below.

$Cl + O_3 \;\text{<====>}\; ClO + O_2$	Reaction 1	$K_1 = k_1 / k_{-1}$
$Br + O_3 \;\text{<====>}\; BrO + O_2$	Reaction 2	$K_2 = k_2 / k_{-2}$
$ClO + BrO \xrightarrow{k_3} Cl + Br + O_2$	Reaction 3	

(a) What is the overall reaction that occurs as a result of this mechanism?

(b) Making the assumption that the third reaction is the rate determining step and that the first two are in rapid equilibrium, what would you predict for the observed overall rate law for this reaction.

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5. A Chemistry 4A student studies the thermodynamics and kinetics of the elementary reaction A + BC ----> AB + C and finds that the internal energy of the products is lower than reactants.

(a) Draw a reaction coordinate diagram for this reaction showing the internal energy of the system vs. reaction coordinate. Clearly label the reactants, products, transition state, change in internal energy ΔE, and both the forward and reverse activation energies.

(b) While studying the kinetics of this reaction, the student observes that the rate depends on temperature as predicted by the Arrhenius rate law. Draw Maxwell-Boltzmann kinetic energy distributions and use them to explain why the rate of reaction depends so dramatically on temperature.

(c) Given that the equilibrium constant for this reaction is 43 and that the forward rate constant is $k_f = 240$ L/mol*sec at 1000 K, calculate the rate constant for the reverse reaction at 1000 K.

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6. Complete and balance the following redox reactions.

acidic

$$Hg_2HPO_4 + Au + Cl^- \longrightarrow Hg + H_2PO_4^- + AuCl_4^-$$

basic

$$HXeO_4^- \longrightarrow XeO_6^{4-} + Xe$$

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7. Malonic acid is a diprotic acid $K_1 = 1.4 \times 10^{-3}$ and $K_2 = 2.0 \times 10^{-6}$. You are given a solution of malonic acid that has an initial concentration of 1 M.

(a) What is the pH of this solution?

(b) Draw a titration curve for the titration of 100 mL of 1 Molar malonic acid with 1 M NaOH. Label the equivalence points and any buffer regions and indicate the pH at each of these points.

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8. The following problem is concerned with Michaelis-Menten enzyme kinetics as described by the following reaction mechanism.

$$E + S \underset{k_{-1}}{\overset{k_1}{<=====>}} ES \xrightarrow{k_2} P$$

k_1 and k_{-1} are very fast (ie. k_1 and k_{-1} are >> k_2)
$k_2 = 100\ s^{-1}$, $K_m = 1.0 \times 10^{-4}$ M at 280 K
$k_2 = 200\ s^{-1}$, $K_m = 1.5 \times 10^{-4}$ M at 300 K

You will hopefully recall that the Michaelis-Menten equations are:

$$v = \frac{v_{max}[S]}{K_m + [S]} \quad \text{where } K_m = (k_2 + k_{-1})/k_1 \text{ and } v_{max} = k_2 E_o$$

(a) Given that [S] = 0.10 M and $[E_O] = 1.0 \times 10^{-5}$ M, calculate the rate of formation of P at 280 K

(b) Calculate the activation energy for k_2.

(c) Give an expression for the equilibrium constant for E + S <===> ES at 280 K and then calculate the equilibrium constant.

(d) What is the standard state Gibbs free energy at 280 K for ES relative to the reactants.

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9. In class on several occasions I showed you the formation of the deep blue colored $Cu(NH_3)_4^{2+}$ complex ion from Cu^{2+} solutions and ammonia. The overall equilibrium describing this reaction in aqueous solution is

$$Cu^{2+} + 4\,NH_3 \text{ ----> } Cu(NH_3)_4^{2+}$$

(a) Use the appended Tables to determine the value of ΔG^o for this reaction.

(b) What is the value of the equilibrium constant at 25° C.

(c) Suppose you add enough very concentrated ammonia to a 0.001 M Cu^{2+} solution make it 0.1 M in ammonia. Once equilibrium is established what will the residual concentration of Cu^{2+} in the solution be?

(d) While you are observing the experiment in part c, the air conditioning failed and the temperature of the room and the solution goes up from 25° C to 35° C. Will this perturbation increase or decrease the residual concentration of Cu^{2+}? Why? Quantitate your answer by calculating the equilibrium constant at 35° C and redetermining the residual concentration of Cu^{2+}.

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10. The following data give the temperature dependence of the rate constant for the reaction

$$N_2O_5 \text{ ----> } 2NO_2 + 0.5\ O_2$$

Temperature	Rate constant k
338 K	$5.1 \times 10^{-3}\ s^{-1}$
328	1.3×10^{-3}
318	5.2×10^{-4}
308	1.3×10^{-4}
298	3.7×10^{-5}
273	7.0×10^{-7}

(a) Use these data to determine the activation energy of the reaction and the Arrhenius preexponential factor. Show your work and method clearly!

(b) What value would you predict for the rate constant at a temperature of 375 K?

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11. In Experiment 9 you used the spectrophotometer to measure a rate constant at different temperatures and hence determine the activation energy of the reaction.

(a) Assume that your measurements were completely accurate except that you made a mistake in determining the highest temperature. Your recorded value was 2 K lower than the actual temperature. This would cause you to report a value of E_a that is (circle the correct answer):

Too large Accurate Too small

(b) What do you believe the largest source of error or uncertainty was in your measurement of the temperature? Explain whether the error caused is always positive, always negative, or randomly positive and negative.

(c) When you used the temperature probe to measure the temperature in the spectrometer cell, you had the option to set the probe on the table or in the constant temperature bath between measurements. Which choice gives the better results? Why?

15

12. You would expect from the Third Law that the entropy of pure crystalline water at a temperature of absolute zero would be zero. It is found instead that there is a residual entropy in these crystals that is 0.82 cal/mol deg. Let's try to understand this observation. As indicated in the Figure in the handout, the water molecules sit in tetrahedral sites in this crystal and each water molecule accepts two hydrogen bonds and donates two hydrogen bonds.

(a) First, qualitatively what do you think might be the physical origin of this increased entropy.

(b) To develop a more quantitative understanding of these observations, it is important to realize that the oxygen atom of each water molecule has four nearest neighbor oxygen atoms from the four closest water molecules. We further assume that each hydrogen can be in one of two positions - on one oxygen or the other. If we consider a mole of ice (N_o molecules or $2N_o$ hydrogens) how many different configurations W of the hydrogen atoms are in principal possible.

(c) The development in part b assumes that all positions are equally likely or energetic. However this treatment includes configurations like H_4O^{++} where all four hydrogens are on the central oxygen, H_3O^+, HO^- and O^{--} as being equivalent to the lowest energy structure H_2O. Show by listing or drawing the various structures that there are 16 different configurations of H atoms about each oxygen.

(d) How many (or what fraction) of these configurations are energetically acceptable in the sense that they have two and only two hydrogens strongly bonded to each oxygen.

(e) Now correct your estimate for W in part b by only counting those configurations that are energetically acceptable.

(f) Now use the expression $S = k \ln W$ to calculate a numerical value for the residual entropy in water ice. Compare this number with the observed value given above. What does this tell you about the structure of water ice.