Chemistry 134 **Your Name:** _____

Prof. Jason Kahn

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

General Chemistry and Energetics

Final Exam (200 points total) **May 16, 2017**

You have 120 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:

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

$K_w = [H^+][HO^-]$ $\quad pH = pK_a + \log [A^-]/[HA]$ $\quad \Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $\quad k_B = 1.38 \times 10^{-23}$ J/K $\quad \ln K_{eq} = (-\Delta H°/R)(1/T) + \Delta S°/R$

$\Delta S = q/T$ $\quad R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$

$S = k_B \ln W$ $\quad \Delta G = \Delta H - T\Delta S$ $\quad \Delta G = \Delta G° + RT\ln Q$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

$°C = °K - 273.15$ $\quad P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\quad E = E° - 2.303(RT/n\mathcal{F})\log_{10} Q$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C $\quad \mathcal{F} = 96500$ C(oulomb)/mole

$\Delta G° = -n\mathcal{F}E°_{cell}$ $\quad \ln k = (-E_a/RT) + \ln A$ $\quad 1$ Volt $= 1$ Joule/Coulomb

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

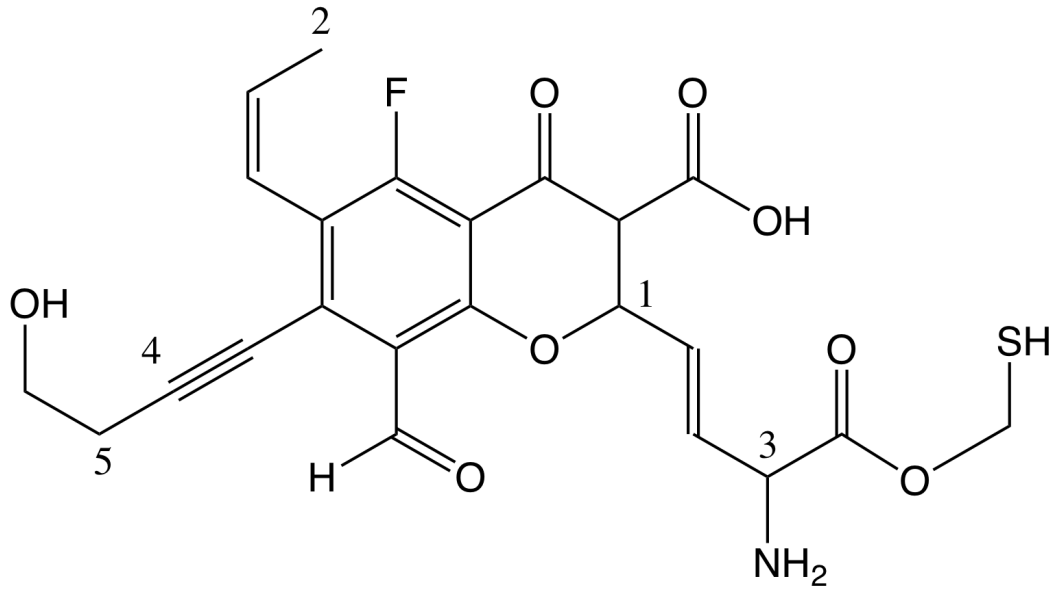
Standard hydrogen electrode: $2\ H^+(aq, 1\ M) + 2\ e^- \rightarrow H_2(g)$ $\quad E°_{red} = 0.000$ V

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. Organic Chemistry (35 pts)

(a; 35 points) Label the amine, aldehyde, ketone, ester, alcohol, and carboxylic acid functional groups in the molecule below. Label *cis* and *trans* alkene moieties, the aromatic ring, and the alkyne moiety. How many hydrogens are attached at each of carbons 1, 2, 3, 4, and 5?

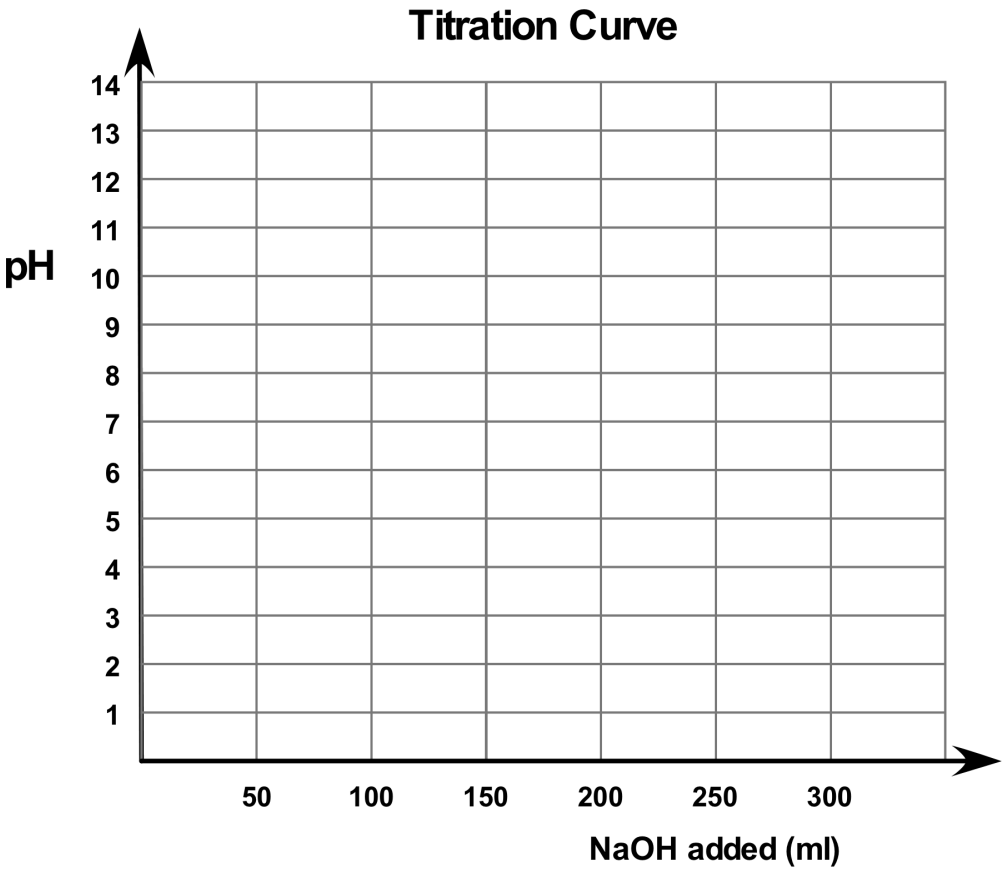


2. Acid-Base chemistry (50 pts)

(a; 20 pts) Calculate the pH of a 0.125 M solution of the monoprotic acid FCH_2COOH, fluoroacetic acid, pK_a 2.59. Assume "*x*" is small. Based on the result, is this a good assumption? Is the true pH more or less than the value you obtained, and how do you know?

Score for the page_____

(b; 30 pts) Draw a titration curve for the titration of 100 ml of a 0.250 M solution of a diprotic acid H_2A, with pKa1 = 3.8 and pKa2 = 6.6, with 0 to 300 ml of 0.250 M NaOH. Anchor points, though you know how to calculate them yourself: The pH of 0.250 M H_2A is about 2.2, and the pH of 0.125 M Na_0A^{2-} point is about 9.8. Label and give the pH values for the beginning, the two half-equivalence points, the two equivalence points, and the 300 ml endpoint of the titration. Indicate the buffer regions.



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3. Electrochemistry (60 pts)

Consider the oxidation of sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}) by permanganate, MnO_4^-, in basic solution. The overall reaction is as follows:

$$2\ MnO_4^-\ (aq) + 3\ SO_3^{2-}\ (aq) + H_2O\ (l) \longrightarrow 2\ MnO_2\ (s) + 3\ SO_4^{2-}\ (aq) + 2\ OH^-(aq)$$

(a; 10 pts) The permanganate is converted to solid manganese dioxide, MnO_2. Figure out the balanced reduction half-reaction for the permanganate. $E°_{red} = +0.59$ V for this process.

(b; 10 pts) Figure out the balanced oxidation half-reaction for $SO_3^{2-} \longrightarrow SO_4^{2}$. $E°_{ox} = +0.92$ V.

(c; 10 pts) Derive the balanced redox reaction above and give values for *n* and $E°_{cell}$.

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(d; 10 pts) Use the Nernst equation to calculate the actual voltage E_{cell} at $[SO_4^{2-}] = 0.178$ M, pH 12, $[MnO_4^-] = 0.200$ M, and $[SO_3^{2-}] = 0.256$ M.

(e; 10 pts) Calculate E_{cell} when 0.245 M of the SO_3^{2-} has reacted.

(f; 10 pts) Calculate E_{cell} when the reaction has reached equilibrium. Do you expect the reaction to go effectively to completion? Explain why or why not.

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5. Chemical Equilibrium (55 pts)

Hydrogen sulfide (H_2S) is a poisonous gas responsible for the delicate aroma of rotten eggs. Its thermal decomposition could be useful in converting H_2S waste from petroleum refining into H_2 gas as well as elemental sulfur; current methods convert the hydrogen to water instead.

$$2\,H_2S\,(g) \rightleftharpoons 2\,H_2\,(g) + S_2\,(g) \quad K_c = 2.2 \times 10^{-4} \text{ at } 1400\text{ K}$$

(a; 5 pts) Write down the expression for Q.

(b; 20 pts) For a sample that initially contains 5.4 M H_2S and no H_2 or S_2, calculate the concentrations of all three gases at equilibrium at 1400 K. Assume that x is small in order to solve the problem, and then state in a few words how you would improve your answer.

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(c; 15 pts) If the reaction mixture is instantly cooled down without changing any concentrations, and the sulfur is condensed and removed, which way will the reaction progress when the temperature is again raised to 1400 K? This suggests one way to improve yield. Could you also improve the yield by carrying out the reaction at much higher pressure? Why or why not?

(d; 15 pts) Write down the equation you would have to solve to determine "x" when the mixture in (*c*) has reached equilibrium again. What order polynomial is it?

Page	Score
2	/55
3	/30
4	/30
5	/30
6	/25
7	/30
Total	**/200**

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