Chemistry 134 **Your Name:** Key

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

General Chemistry and Energetics

<u>Final Exam (200 points total)</u>

JK 5/16/17

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:

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

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

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

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

$S = k_B \ln W$ $\Delta G = \Delta H - T\Delta S$ $\Delta G = \Delta G^\circ + RT\ln Q$

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

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

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

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

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

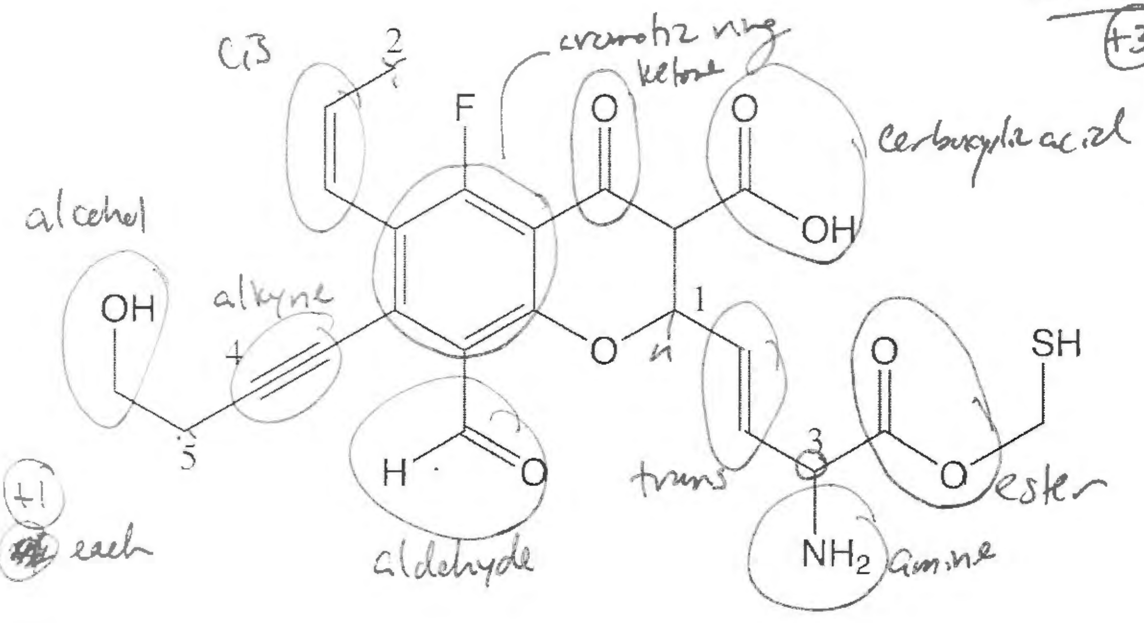
<u>Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:</u>

"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?

Labels: (+3) each
no partial credit
= 30



1: 1
2: 3
3: 1
4: 0
5: 2

(+1) each

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?

(+5)

	FCH_2COOH	$FCH_2COO^{\ominus}$	H^+
I	0.125M	0	0
C	$-x$	$+x$	$+x$
E	$0.125-x$	x	x

$pK_a = 2.59$

$$K_a = 10^{-2.59} = \boxed{2.57\times10^{-3} = \frac{x^2}{\underbrace{0.125-x}_{\simeq 0.125}}}$$ (+3)

$$x \approx \sqrt{K_a \cdot 0.125} = \sqrt{3.21\times10^{-4}} = 0.0179$$

(+3)

$pH = -\log_{10} x = 1.75$

0.0179 is about 10% of C_0 – not a great assumption. (+3)

(+3)

True pH is higher – lower $[H^+]$, b/c the value we got is based on a non-dissociated $[HA]$ that is too high. (+3)

Score for the page________________ /55

(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_2A^{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.

oops – should have been 0.083 M – makes very little difference to overall appearance

1st e.p. – $pH = \frac{1}{2}(pK_{a1} + pK_{a2}) = \frac{1}{2}(3.8+6.6) = 5.2$

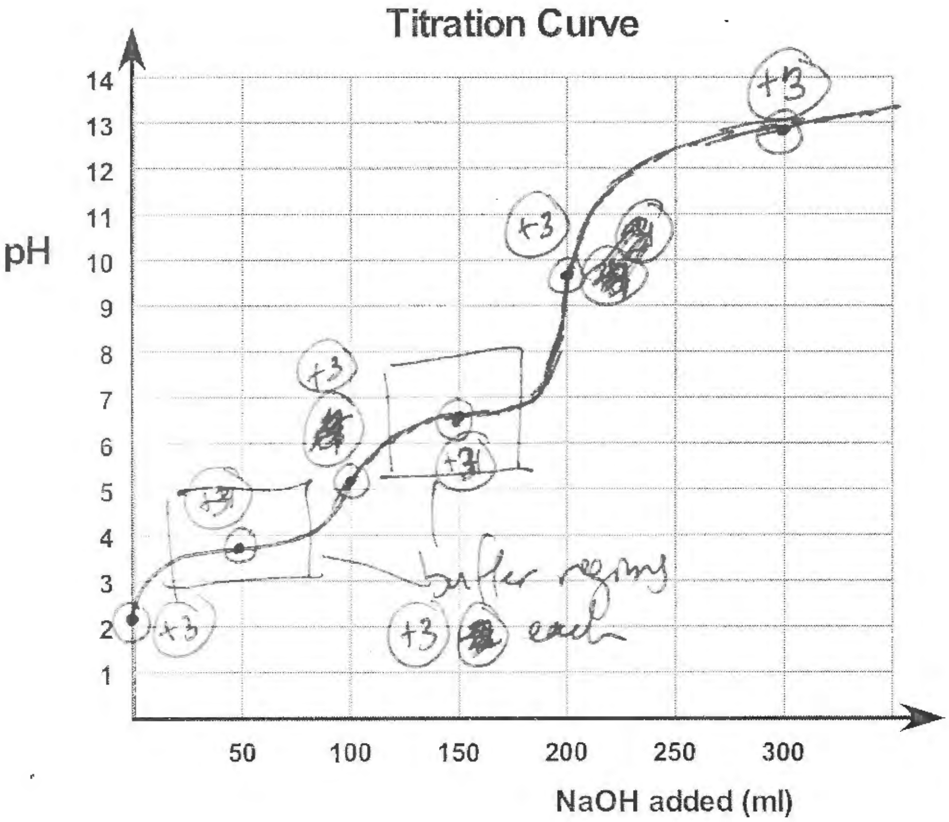
2nd e.p. = pH of Na_2A^{2-}

~~pOHz~~ $[HO^-] = \sqrt{K_b \cdot 0.083} = \sqrt{10^{-7.4} \cdot 0.083}$

$= 5.75 \times 10^{-5}$ so pOH = 4.24, pH = 9.76

300 ml: we have added 100 ml of 0.250 M NaOH in excess of ~~A~~ H_2A, so xs $[HO^-] = \frac{100}{300} \cdot 0.250 = 0.083$ M, ~~pH~~

pOH = 1.08, pH = 12.92



+3 for any titration

+3 for correct concavity

total +30

For a good monoprotic titration: 15 pts.

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.

$MnO_4^- \rightarrow MnO_2$ Mn balanced ✓ Ox#! +7 → +4 - reduction ✓

Balance O's: $MnO_4^- \rightarrow MnO_2 + 2\,H_2O$ ⊕2 +3 for any ½-rxn

Balance H's: $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2\,H_2O$ (+2)

Balance e⁻: $MnO_4^- + 4H^+ + 3e^- \xrightarrow{(+2)} MnO_2 + 2H_2O$ — reduction ✓ +7 for acidic soln

$\quad\quad\quad 4OH^- \quad\quad\quad\quad\quad +4HO^-$

Convert to basic: $MnO_4^- + 2H_2O + 3e^- \xrightarrow{(+4)} MnO_2 + 4\,HO^-$ (+10 for just this)

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

$SO_3^{2-} \rightarrow SO_4^{2-}$ Ox # of S: 4 → ~~4~~ 6 oxidation ✓

(+2) $SO_3^{2-} + H_2O \rightarrow SO_4^{2-}$

(+2) $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2\,H^+$ (+2) - oxidation ✓

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2\,H^+ + 2e^-$

$\quad\quad +2HO^- \quad\quad\quad\quad +2HO^-$

(+4) $SO_3^{2-} + 2\,HO^- \rightarrow SO_4^{2-} + H_2O + 2e^-$

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

need to balance e⁻ ~~so by~~

~~(+2)~~ (+1) $2\,MnO_4^- + 4\,H_2O + 6e^- \rightarrow 2\,MnO_2 +$ ~~[illegible]~~ 8 HO^-

~~(+2)~~ (+1) $3\,SO_3^{2-} + 6\,HO^- \longrightarrow 3\,SO_4^{2-} + 3\,H_2O + 6e^-$ (+2)

(+1) $2\,MnO_4^- + 3\,SO_3^{2-} + H_2O \longrightarrow 2\,MnO_2 + 3\,SO_4^{2-} + 2\,HO^-$ ✓

$E°_{cell} = E°_{ox} + E°_{red} = 0.92\,V + 0.59\,V = \underline{1.51\,V}$ (+3)

(+2) for idea

Score for the page________

/30

(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.

(+3) for idea of Nernst

$$E_{cell} = E^0_{cell} - \frac{0.0592\,V}{6}\log_{10}\left[\frac{[SO_4^{2-}]^3[HO^-]^2\cancelto{1}{[MnO_2]^2}}{[MnO_4^-]^2[SO_3^{2-}]^3\cancelto{1}{[H_2O]}}\right]$$

(+2) for idea of Q

$$= 1.51V - 0.00987\,V\log_{10}\underbrace{\frac{(0.178)^3(10^{-2})^2}{(0.200)^2(0.256)^3}}_{(+2)\text{ for plugging in \#'s}}\Big\}\,8.40\times10^{-4}$$

$$= 1.51V + 0.0303V = \underline{1.54V}$$

(+3) for answer

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

(+2) for idea of calculating new [ ]'s

$[SO_3^{2-}] = 0.256 - 0.245 = 0.011$ M (+2)

$[SO_4^{2-}] = 0.178 + 0.245 = 0.423$ M

$[MnO_4^-] = 0.200\,M - \frac{2}{3}(0.245\,M) = 0.03667$ M

[+2 pts for just plugging in .245 instead of .256]

$[MnO_2] \rightarrow$ doesn't matter

for plugging in (+3) full credit for consistent w/ (d)

$[HO^-] = 0.0100 + \frac{2}{3}(0.245M) = 0.173$ M

$$E_{cell} = 1.51V - 0.00987V\log_{10}\underbrace{\frac{(0.423)^3(0.173)^2}{(0.0367)^2(0.011)^3}}_{\rightarrow 1.26\times10^{6}!} = \underline{1.45V}$$ (+3)

(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.

(+3) $E_{cell} = 0$ at equilibrium! → i.e. $Q \rightarrow \infty$

+5 for an intelligent but wrong limiting reagent answer

(+3) Yes it will go to completion

We showed that Q going from 8×10^{-4} to 1×10^{6} changes E_{cell} by only 0.09V and the voltage is still very (+). (+2) To get $E_{cell} = 0$ we would need $Q = 10^{150}$!

(+2) for any calculation or reference to #'s.

Score for the page____________ /30

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.

$$Q = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

(+5)

(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.

(+3) (+[illegible])

	H_2S	H_2	S_2
I	5.4	0	0
C	$-2x$	$+2x$	$+x$
E	$5.4-2x$	$2x$	x

(+3) for plugging in = cubic eq'n -

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]} = \frac{(2x)^2(x)}{(5.4-2x)^2} \approx \frac{4x^3}{5.4^2} = 2.2\times10^{-4}$$

(+2) to [illegible]

$$x \simeq \sqrt[3]{1.6038\times10^{-3}} = 0.117\text{ M}$$

(+2) to improve

(+2) $[H_2S] = 5.17$ M

(+2) $[H_2] = 0.234$ M

(+2) $[S_2] = 0.117$ M

$Q = 2.4\times10^{-4}$ ~ 10% off.

To improve estimate for "x" -

- solve the cubic
- numerical solution to equation w/ e.g. Solver
- Wolfram alpha
- Successive approximation

(+4) for any

Score for the page /25

(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?

+3

- Le Chatelier – we have removed product – it will go forward
  [so improve yield by constant removal of S_2 (actually S_8)]

+4

- Going to high pressure will drive rxn backward b/c we are increasing moles of gas – will not work to ↑ yield.

+4 +4

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

	H_2S	H_2	S_2
(+4) I	5.17 M	0.234	~~0.117~~ → 0
(+5) C	$-2x$	$+2x$	$+x$
E	$5.17-2x$	$0.234+2x$	x

~~+5~~ +4

$$\boxed{K_c = 2.2\times10^{-4} = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{(0.234+2x)^2(x)}{(5.17-2x)^2}}$$

+4 for idea that K_c is still the same

+3 3rd order polynomial as before

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

Score for the page /30