Chemistry 134 **Your Name:** -Key-

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

General Chemistry and Energetics

Final Exam (150 points total) **December 19, 2016**

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:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [HA][HO^-]/[A^-]$
$K_w = [H^+][HO^-]$	$pH = pK_a + \log [A^-]/[HA]$	$\Delta G° = -RT\ln K_{eq}$
$R = 0.08206$ L·atm/mole K	$k_B = 1.38 \times 10^{-23}$ J/K	$\ln K_{eq} = (-\Delta H°/R)(1/T) + \Delta S°/R$
$\Delta S = q/T$	$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$	
$S = k_B \ln W$	$\Delta G = \Delta H - T\Delta S$	$\Delta G = \Delta G° + RT\ln Q$

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

$°C = °K - 273.15$	$P(v)dv = Cv^2 exp(-mv^2/2kT)$	$E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$
$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C		$\mathcal{F} = 96500$ C(oulomb)/mole
$\Delta G° = -n\mathcal{F}E°_{cell}$	$\ln k = (-E_a/RT) + \ln A$	1 Volt = 1 Joule/Coulomb
$[A] = [A]_0 - kt$	$\ln[A] = \ln[A]_0 - kt$	$1/[A] = 1/[A]_0 + 2kt$

Standard hydrogen electrode: $2\,H^+(aq, 1\,M) + 2\,e^- \rightarrow H_2(g)$ $E°_{red} = 0.000$ 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 (46 pts)

(a; 6 pts) Why does carbon get a branch of chemistry to itself? Why not Si, or Al, or P, or some other deserving element? What makes carbon unique? Answer in two phrases or sentences.

+3 – Carbon makes 4 bonds so extended structures are possible

+3 – C-H, C-O, C-N, C-C, C-S bonds are of comparable strength

+3 – Extended structures aren't just minerals –

any two (+ may be other possibilities)

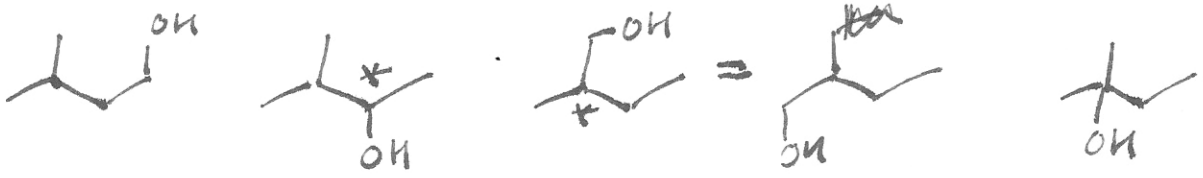
+1 (has high electroneg.

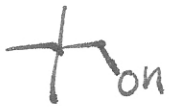
+2 makes up our bodies

+3 forms more compounds than anything else

+3 many oxidation states

(b; 10 pts) Draw two examples of a branched chain alcohol with molecular formula $C_5H_{12}O$. (There are at least 5 possible answers, not including stereochemistry.)





+3 for any thing with an –OH

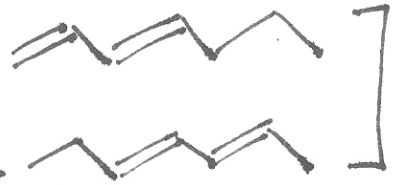
+3 for 5-carbon alcohols w/ one –OH

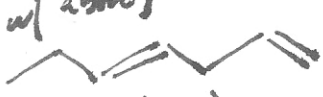
+2 for each correct structure

* I suppose ~~stereo~~ stereoisomers count as correct answers

(c; 10 pts) Draw *trans*-3-*n*-heptene, C_7H_{14}. Draw one of the three possible products of oxidizing (i.e. removing 2 H's from) *trans*-3-*n*-heptene, to make a molecule with molecular formula C_7H_{12} containing two conjugated double bonds.

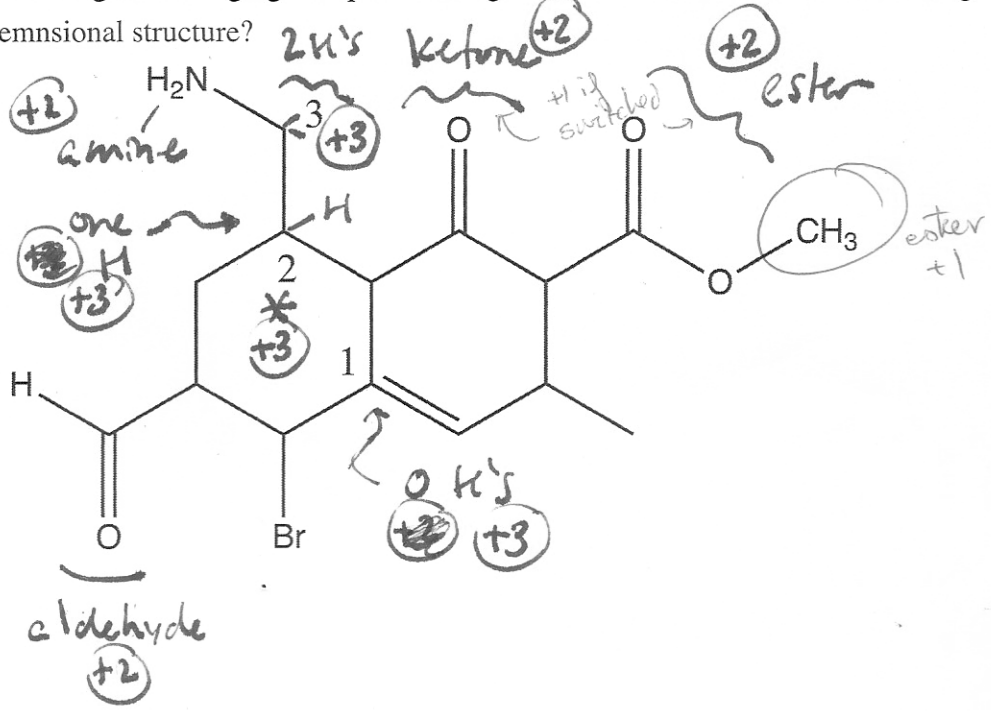
+5  trans-3-heptene (vs. cis  (+2))

+5 for either  2 products w/ conjugated double bonds (+3 for any alkene)

(full credit if consistent w/ above)  (+2)] non-conjugated

Score for the page 126

(d; 20 points) Identify the amine, aldehyde, ketone, and ester functional groups in the molecule below. How many hydrogens are attached at each of carbons 1, 2, and 3? Which one of those three carbons is a "stereocenter," meaning that changing the spatial arrangement of bonds at that carbon would give a different 3-dimemnsional structure?



2. Acid-Base chemistry (36 pts)

(a; 8 pts) Calculate the pH of a 0.100 M solution of the weak monoprotic acid HCOOH, formic acid, pK_a 3.62. Assume "x" is small.

	HCOOH	$HCOO^-$	H^+
I	0.100 M	0	0
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	x

(+3) $\frac{x^2}{0.100-x} = K_a = 10^{-3.62} = 2.40\times10^{-4}$

$x^2 = (2.40\times10^{-4} \cdot 0.100)$ (+2)

$x = 0.00490\ M = [H^+]$

(<5% of 0.100)

$pH = -\log([H^+]) = 2.31$ (+3)

Score for the page ____/28

Consider the titration curve for the titration of 100 ml of 0.1 M formic acid with 0 to 150 ml of strong base, 0.1 M NaOH.

(b; 12 pts) Write down the base dissociation equation for formate ion, $HCOO^-$. Use it to calculate the pH at the equivalence point of the titration (100 ml of NaOH added). Again, assume "y" (not the same as "x") is small. Before you start, you know the pH is >7. Why? → It's a strong base plus a weak acid — must be basic (+2)

(+4 for either)

$$HCOO^- + H_2O \rightleftharpoons HCOOH + HO^-$$

$$K_b = \frac{[HCOOH][HO^-]}{[HCOO^-]} = \frac{10^{-14}}{K_a} = 4.17\times10^{-11}$$ (+2)

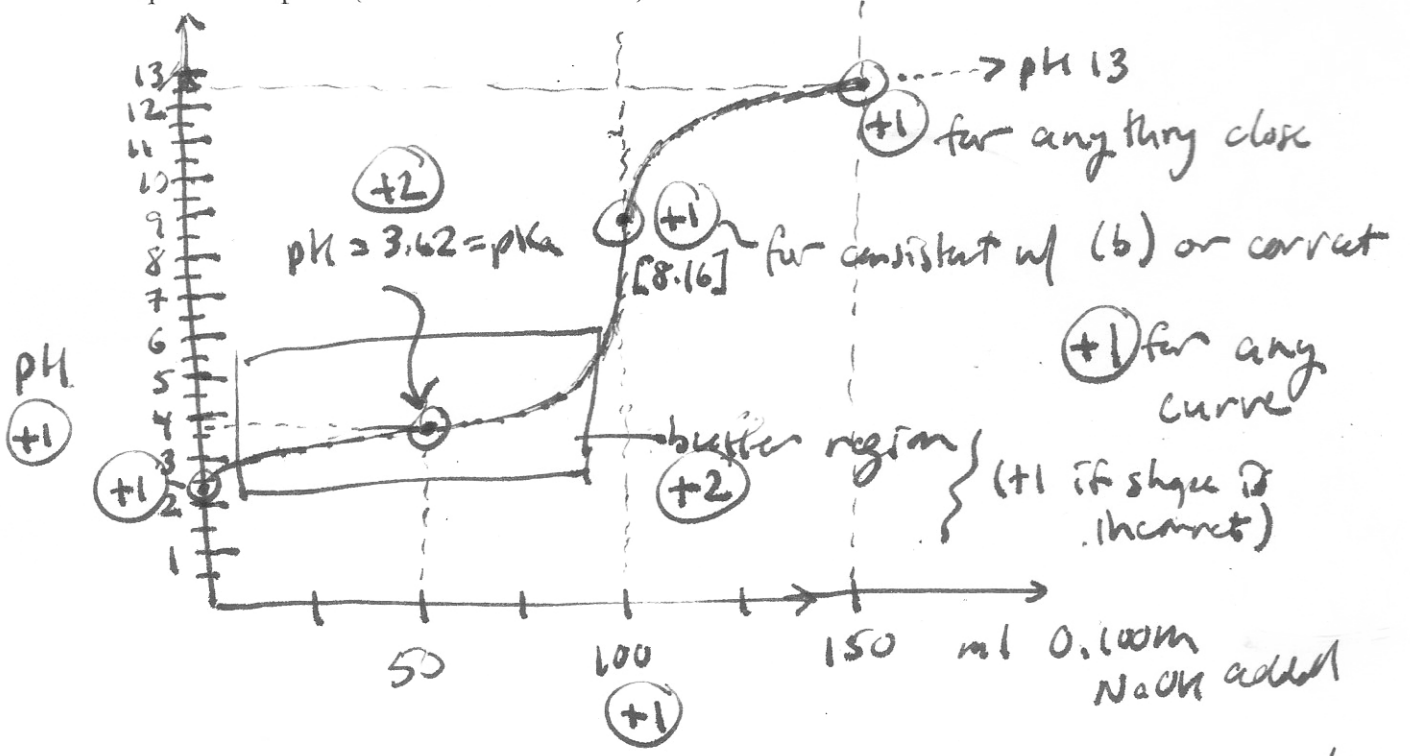
Total volume is now 200 ml, so $\frac{y^2}{0.050 - y} = 4.17\times10^{-11}$

$y \approx \sqrt{0.050 \times 4.17\times10^{-11}} = 1.44\times10^{-6} = [HO^-]$ (+2)

So pOH = 5.84, pH = 14 − 5.84 = 8.16 (+2)

reasonable guess +1

(c; 10 pts) Sketch the titration curve described above. Label the buffer region and state the pH at the half-equivalence point (50 ml of NaOH added).



Score for the page 22

(d; 6 pts) What is the approximate pH at the end of the titration, when we have added 150 ml of 0.1 M NaOH? Hint: I call the end of the titration "adding base to salt." (+3)

50 ml extra NaOH diluted to 250 ml → 0.020 M NaOH left over after neutralizing the HCOOH – once all of the HCOOH is $HCOO^-$, it does not affect pH.

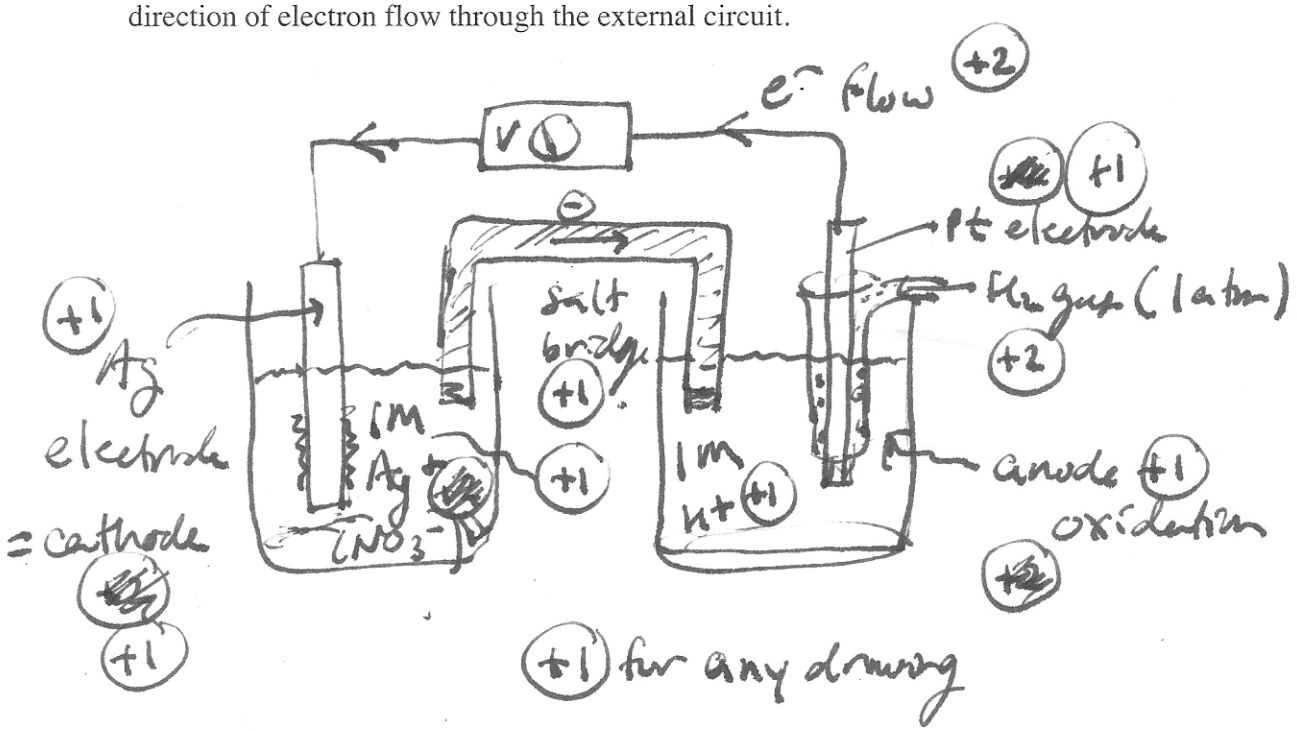
So at this point solution is 40 mM $HCOO^-$, no HCOOH, 0.02 M NaOH → pOH = 1.70, pH = 12.30 (+3)

pH = 13 +2

3. Electrochemistry (45 pts)

Consider a Ag(s)/$Ag^+(aq)$ half cell set up by one of your lab partners, hooked up to what your other lab partner told you is a Standard Hydrogen Electrode (SHE). Based on the standard reduction potential tables, the voltage should be +0.80 V for the reduction of Ag^+ (causing it to plate out on the electrode), with accompanying oxidation of H_2 to H^+.

(a; 12 pts) Sketch the setup, including labeling the anode, cathode, and salt bridge and indicating the direction of electron flow through the external circuit.



Score for the page 18

(b; 8 pts) Write down each half-reaction and the balanced overall redox reaction.

$\times 2\left[Ag^+(aq) + 1e^- \rightarrow Ag(s) \right]$ reduction (+2)

$H_2(gas) \rightarrow 2H^+(aq) + 2e^-$ oxidation (+2)

$2Ag^+(aq) + H_2^{(g)} \rightarrow 2H^+(aq) + 2Ag(s)$ (+4)

[+2 for reversed overall rxn]

Instead of 0.80V, you measure 0.85 V. You suspect that one, but only one, of the aqueous components was prepared incorrectly, i.e. that either the Ag^+ concentration or the H^+ concentration is not at the standard state. [We ignore any possible overpotential or conductivity complications.]

(c; 8 pts) Calculate the non-standard Ag^+ concentration that would be required for you to observe 0.85 V, assuming that the SHE was set up correctly.

(+3) $E_{cell} = E^\circ_{cell} - \frac{0.0592\,V}{n(=2)} \log_{10} Q$

(+2) $0.85V = 0.80V - 0.0296\,V \log_{10} \frac{[H^+]^2 \rightarrow = 1M}{[Ag^+]^2 \rightarrow = ?}$

$-\frac{0.05}{0.0296} = \log_{10} \frac{1}{[Ag^+]^2} = -2 \log([Ag^+])$ (+1)

(+1) $\log([Ag^+]) = 0.845$ $[Ag^+] = 6.99\,M$

[Solubility of $AgNO_3$ ~ 1.5 M at 25 °C.]

(d; 6 pts) Calculate the pH of the non-standard hydrogen electrode (denoted the %$@#*&%$-NSHE) that would be required to give 0.85 V, assuming that the Ag(*s*)/Ag^+(*aq*) half-cell was set up correctly.

(+3) $0.85V = 0.80V - 0.0296\,V \cdot \log_{10} \frac{[H^+]^2}{1}$

$\log_{10}([H^+]) = -0.845$

so $pH = 0.85$ (+3)

The SHE is pH = 0 (1M $[H^+]$).

Score for the page 22/22

(e; 5 pts) Which half-cell is the likely culprit: explain your reasoning?

+2 - The SHE

+3 - It's a lot easier to make ~0.1 M H^+ instead of 1 M — to use 7× more Ag^+ than expected would require a huge measuring error — esp. since $AgNO_3$ is not that soluble!

(f; 6 pts) Where does the energy released in combustion come from? In terms of redox, explain why burning natural gas provides about twice as much free energy per carbon atom released than burning coal or wood.

+3 for either

- Energy comes from <u>making bonds</u> — stable CO_2 and H_2O molecules —

— <u>Or</u> — Energy comes from <u>giving electrons to electronegative oxygen</u>. "moving electrons" +2

+3

- CH_4 gives 8 e^- per carbon to O_2 upon combustion —
- Coal = C(s) gives 4 e^- per carbon
- Wood ≅ $C_n(H_2O)_n$ is the same

Score for the page 11

5. Chemical Equilibrium (23 pts)

The equilibrium constant for the endothermic reaction $H_2(g) + I_2(s) \rightleftharpoons 2\ HI(g)$ is $K_p = 0.345$, at 25 °C.

(a; 5 pts) Gaseous H_2 is added to excess solid iodine and the equilibrium partial pressure of H_2 is found to be $P_{H2} = 0.87$ atm. What is the equilibrium partial pressure of HI at 25 °C?

$K_p = \frac{P_{HI}^2}{P_{H_2}}$ (+2)

$0.345 = \frac{P_{HI}^2}{0.87}$ (+2) so $P_{HI} = \sqrt{0.345 \times 0.87} = 0.548$ atm (+1)

(b; 10 pts) Excess solid I_2 is added to a container filled with 3.50 atm of H_2, with the vessel maintained at constant volume and 25 °C. Set up but do not solve the quadratic equation that would give you the final partial pressure of HI. Will the final total pressure in the container be more or less than 3.50 atm (you do not need to do a calculation to answer)?

	I_2	H_2	HI
I	(xs)	3.50 atm	0
C	$-x$	$-x$	$+2x$
E	(some)	$3.50-x$	$2x$

(+3 for table)
↳ gives credit for defn of $P_{HI} = 2x$

$0.345 = \frac{(2x)^2}{3.50 - x}$ where $P_{HI} = 2x$ (+7) (+4 for eq'n w/out defn of x)

This gives $(0.345)(3.50 - x) = 4x^2$

$4x^2 + 0.345x - 0.345 - 3.50 = 0$ (+4 out of 7 for missing the "±")

$x = 0.508$

not needed $P_{[HI]} = 1.016$ atm

~~$P_{H_2} = 2.992$ atm~~

The pressure will be >3.50 atm b/c (+3)

Any H_2 that reacts produces 2x that much HI.

Score for the page 15

(c; 8 pts) If the volume of the container is increased at constant temperature, which way will the equilibrium shift, and why? If the temperature is increased, will the equilibrium constant increase or decrease?

V↑ ⇒ P_{H_2} and P_{HI} ↓ ⇒ equilibrium shifts to the right (+2) to ↑ total pressure. (And $Q < K$ after the volume increase.) (+3) [or give a rate explanation — ↓ rate of HI → H_2 and I_2] (+2)

If T↑, Keq ↓ b/c we are told that the reaction is endothermic — heat is a reactant. (+1)

Page	Score
2	/26
3	/28
4	/22
5	/18
6	/22
7	/11
8	/15
9	/8
Total	**/150**

Score for the page 18