Chemistry 134
Prof. Jason Kahn
University of Maryland, College Park
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:

\[ K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{pH} = -\log([H^+]) \quad K_b = \frac{[HA][OH^-]}{[A^-]} \]

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

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

\[ \Delta S = q/T \quad R = 8.314 \text{ J/mole K} \quad 1.987 \text{ cal/mole K} = N_A k_B \]

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

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

\[ ^\circ C = ^\circ K - 273.15 \quad P(v)dv = Cv^2 \exp(-mv^2/2kT) \quad E = E^\circ - 2.303(RT/nF)\ln Q \]

\[ 2.303RT/F = 0.0592 \text{ Volts at 25 } ^\circ C \quad F = 96500 \text{ C(oulomb)/mole} \]

\[ \Delta G^\circ = -nF E^\circ_{cell} \quad \ln k = (-E_q/RT) + \ln A \quad 1 \text{ Volt} = 1 \text{ Joule/Coulomb} \]

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

Standard hydrogen electrode: \[ 2 \text{ H}^+ (aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2 (g) \quad E^\circ_{red} = 0.000 \text{ V} \]

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 infinite structures are possible
+3 C-N, C-O, C-N, C-C, C-S bonds are of comparable strength
+3 Extended structures aren't just minerals
+1 (can high electrical
+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 C₅H₁₀O. (There are at least 5 possible answers, not including stereochemistry.)

(c; 10 pts) Draw trans-3-n-heptene, C₇H₁₄. 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 C₇H₁₃ containing two conjugated double bonds.

Score for the page 26
(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-dimensionsal 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, pKₐ 3.62. Assume “x” is small.

\[
\begin{align*}
\text{I} & \quad \text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{OH}^- \\
\text{C} & \quad -x + x + x \\
\text{E} & \quad 0.100 - x + x + x
\end{align*}
\]

\[
\frac{x^2}{0.100 - x} = K_a = 10^{-3.62} = 2.40 \times 10^{-4}
\]

\[
x^2 = (2.40 \times 10^{-4} \times 0.100) + 2
\]

\[
x = 0.00490 \text{ M} = [\text{H}^+] \\
(<5\% \text{ of } 0.100)
\]

\[
\text{pK}_a = -\log([\text{H}^+]) = 2.31
\]

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?

\[
K_b = \frac{[\text{HCOOH}][\text{H}^+]}{[\text{HCOO}^-]} = \frac{10^{-14}}{K_a} = 4.17 \times 10^{-11}
\]

Total volume is now 200 ml, so

\[
y^2 = 4.17 \times 10^{-11}
\]

\[
y = \sqrt{4.17 \times 10^{-11}} = 2.05 \times 10^{-6} = [\text{H}^+]\]

So \(pH = 5.84\), \(pH = 14 - 5.84 = 8.16\). 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 122.
(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."

\[ \text{sum 1 extra NaOH diluted to 250 ml} \rightarrow 0.020 M \text{ NaOH left} \]

over after neutralizing the \( \text{HCOON}^- \) - once all of the \( \text{HCOON^-} \) is \( \text{HCOO^-} \), it does not affect pH.

So at this point solution is 40 mm \( \text{HCOO^-} \), v 0 \( \text{HCOON^-} \), 0.02m \( \text{NaOH} \) \( \text{pH 12.30} \)

\[ \text{pH = 13, } +2 \]

3. Electrochemistry (45 pts)

Consider a \( \text{Ag(s)/Ag}^+(aq) \) 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 \( \text{Ag}^+ \) (causing it to plate out on the electrode), with accompanying oxidation of \( \text{H}_2 \) to \( \text{H}^+ \).

(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.

\[ 2 \left[ Ag^+ (aq) + e^- \rightarrow Ag (s) \right] \text{ reaction } +2 \]

\[ H_2 \text{ (gas)} \rightarrow 2 H^+ (aq) + 2e^- \text{ oxidation } +2 \]

\[ 2 \left[ Ag^+ (aq) + H_2 (g) \rightarrow 2 H^+ (aq) + 2 Ag (s) \right] \text{ balanced overall reaction } +4 \]

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.

\[ E_{cell} = E^\circ_{cell} - \frac{0.0592 V \log_{10} Q}{nF} \]

\[ 0.85V = 0.80V - 0.0296V \log_{10} \left[ \frac{[H^+]^2}{[Ag^+]} \right] \]

\[ \frac{0.05}{0.0296} = \log_{10} \left[ \frac{[H^+]^2}{[Ag^+]^2} \right] = -2 \log (\left[ Ag^+ \right]) \]

\[ \log (\left[ Ag^+ \right]) = 0.845 \]

\[ \left[ Ag^+ \right] = 6.99 \text{ M at } 25^\circ C. \]

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

\[ 0.85V = 0.80V - 0.0296V \log_{10} \frac{[H^+]}{1} \]

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

\[ \text{So } pH = 0.85 \]

The SHE is pH = 0 (1M [H⁺]).
(e; 5 pts) Which half-cell is the likely culprit: explain your reasoning?

+2
- The SH
+3
- It's a lot easier to make 0.1M H^+ instead of 1M -

+3
- to use 7x 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 more free energy per carbon atom released than burning coal or wood.

+3
- Energy comes from making bonds -- stable CO_2 and H_2O molecules.
- Energy comes from giving electrons to electronegative oxygen.

+3
- CH_4 has 8 e^- per carbon to O_2 upon combustion.
- Coal = C(s) gives 4 e^- per carbon
- Wood = C_n(H_2O)_m is the same.
5. Chemical Equilibrium (23 pts)
The equilibrium constant for the endothermic reaction \( H_2(g) + I_2(s) \rightleftharpoons 2 \text{HI}(g) \) is \( K_v = 0.345 \), at 25 \(^\circ\)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 \( P_{H_2} = 0.87 \) atm. What is the equilibrium partial pressure of \( \text{HI} \) at 25 \(^\circ\)C?

\[
K_v = \frac{P_{\text{HI}}^2}{P_{H_2}}
\]

\[
0.345 = \frac{P_{\text{HI}}^2}{0.87} \quad \text{so} \quad P_{\text{HI}} = \sqrt{0.345 \times 0.87} = 0.548 \text{ atm}
\]

(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 \(^\circ\)C. Set up but do not solve the quadratic equation that would give you the final partial pressure of \( \text{HI} \). 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)?

\[
I \quad \begin{array}{ccc}
(\times 5) & 3.50 \text{ atm} & 0 \\
C & -x & -x & +2x \\
E & \text{solid} & 3.50-x & 2x \\
\end{array}
\]

\[
0.345 = \frac{(2x)^2}{3.50 - x} \quad \text{where} \quad P_{H_2} = 2x
\]

\[
\frac{0.345(3.50-x)}{4x} = 4x^2
\]

\[
4x^2 + 0.345x - 0.345 \cdot 3.50 = 0
\]

\[
x = 0.508
\]

\[
P_{\text{HI}} = 1.016 \text{ atm}
\]

\[
P_{\text{HI}} = 2.992 \text{ atm}
\]

The pressure will be \( > 3.50 \) atm.

Any \( H_2 \) that reacts produces \( 2x \) that much \( \text{HI} \).

Score for the page: 115
(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?

\[ V^0 \Rightarrow P_{Hz} \text{ and } P_{Hz} + \Rightarrow \text{equilibrium shifts to the right to total pressure.} \text{ And } Q < K \text{ after the volume increase.} \]

For a rate explanation, rate of Hz - Hz + Hz.

If T \( \uparrow \), Keq \( \uparrow \) if we are told that the reaction is endothermic; heat is a reactant.

<table>
<thead>
<tr>
<th>Page</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
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<td>7</td>
<td>11</td>
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<td>15</td>
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<td>9</td>
<td>8</td>
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<td>Total</td>
<td>150</td>
</tr>
</tbody>
</table>

Score for the page: 8