Chemistry 271, Section 22xx
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University of Maryland, College Park

Your Name: Key ←

Your SID #: ←

Your Section #: (time + day okay) ←

General Chemistry and Energetics
Exam I (100 points total)

October 5, 2009

N = 150 + 1

You have 50 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. 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:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [HA][HO^-]/[A^-]$
$F = ma$	$e^{i\pi} + 1 = 0$	$PV = nRT$
$K_w = [H^+][HO^-]$	$pH = pK_a + \log [A^-]/[HA]$	$pI = (pK_{a1}+pK_{a2})/2$
$R = 0.08206$ L·atm/mole K	0 °C = 273.15 K	

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."

write out and sign !

(3 pts extra credit for filling out this page accurately and completely)

1. (20 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) The Henderson-Hasselbach relationship is

(a) Always true, not always useful
(b) A useful shortcut for calculating pH when either [HA] or [A-] is very small relative to [H+] or [HO-]
(c) Useful especially for strong acids and bases – No!
(d) Equivalent to the water self-dissociation equilibrium
(e) (a) and (c)

(b; 4 pts) At equilibrium,

(a) The concentrations of reactants and products remain constant – yes
(b) The rates of the forward and reverse reactions are zero – no!
(c) The rates of the forward and reverse reactions are equal – yes
(d) All molecular motion has stopped – no!
(e) (a) and (c)

(c; 4 pts) The relationship $K_a \cdot K_b = K_w$ arises because

(a) It refers to protonation and deprotonation of the same intermediate state of a polyprotic acid
(b) The K_a and K_b equilibria add to give the water self-dissociation equilibrium
(c) Mixing acid and base gives water
(d) K_a and K_b are simply the same reaction written in forward and reverse directions
(e) None of the above

(d; 4 pts) At high pH, enzymes can cease to work because

(a) The protein unfolds
(b) A residue acting as a base is protonated – no
(c) A residue acting as base is deprotonated – no
(d) A residue acting as an acid is deprotonated
(e) (a) and/or (d)

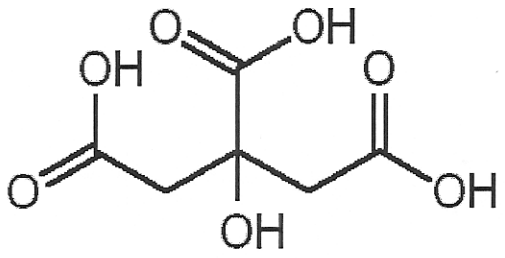
(e; 4 pts) The definition of an ideal gas is that

(a) It is completely unreactive – no
(b) It exerts pressure on the container only because the particles repel each other → they ignore each other
(c) Its temperature is inversely proportional to pressure at constant volume PV=nRT
(d) It condenses to a liquid at low temperature – real gases do this!
(e) None of the above

Score for the page_____

2. (45 pts) Acid-base chemistry

Consider the tricarboxylic acid citric acid drawn at the right in its fully protonated (pH 0) form. Its pK_as are 3.13, 4.76, and 7.40 (actually the last one is 5.40, but I changed it for this problem so that you can assume that only the pK_a closest to the pH is relevant).



(a; 10 pts) What is the pH of a 0.150 M solution of citric acid?

Equilibrium is $H_3C \rightleftharpoons H_2C^- + H^+$ C = citrate

+3 $K_a = 10^{-3.13} = \frac{[H^+][H_2C^-]}{[H_3C]}$ – only first eq. is relevant to pH of acid alone in H_2O

+2 $7.41\times10^{-4} = \frac{x^2}{0.150\,M - x} \approx \frac{x^2}{0.150\,M}$ $x = \sqrt{0.150 \times 7.41\times10^{-4}}$

Assume x is negligible in the denominator but state how you would get a more exact answer

+3 $x = 0.0105$ not negligible

$pH = -\log(0.0105) = \boxed{1.98}$

– (<< 2nd pKa so 2nd pKa doesn't contribute ✓)

+2 – would improve by solving the quadratic or successive approximations

(b; 3 pts) What is the average net charge on citrate at pH = 4.76?

First proton is ~entirely removed. Average charge = $\underline{-1\frac{1}{2}}$. +3

(or slightly less negative if 4.76 too)

(c; 6 pts) Does citrate have a pI between 1 and 13? If it does, what is it? If it doesn't, why not?

+3 No, it is always either ⊖ or neutral, so there is no pH at which charge = 0. +3

Score for the page_____

(d; 7 pts) Use the H-H relationship to calculate the pH of a solution of 0.150 M total citric acid/citrate after addition of 0.275 M NaOH. Assume that the pKa closest to the pH is relevant.

+2 $pH = pK_a + \log \frac{[A^-]}{[HA]}$ $0.150 < 0.275 < 0.300$ – closest to 2nd pKa

$= 4.76 + \log \frac{0.125}{0.025} = 4.76 + \log 5 = 5.46$

+2 (for picking the correct pKa) +2 +1 (okay if it's consistent)

e

(f; 3 pts) Assuming the H-H still applies, what would the pH be if you diluted the above solution 10-fold (to 0.015M citrate)?

the same – 5.46 (consistent w/ above)

f

(g; 5 pts) If you diluted the solution further 10000-fold (to 1.5×10^{-6} M), would the pH go up or down, and why (qualitatively)?

+2

The pH would go up (toward 7) –

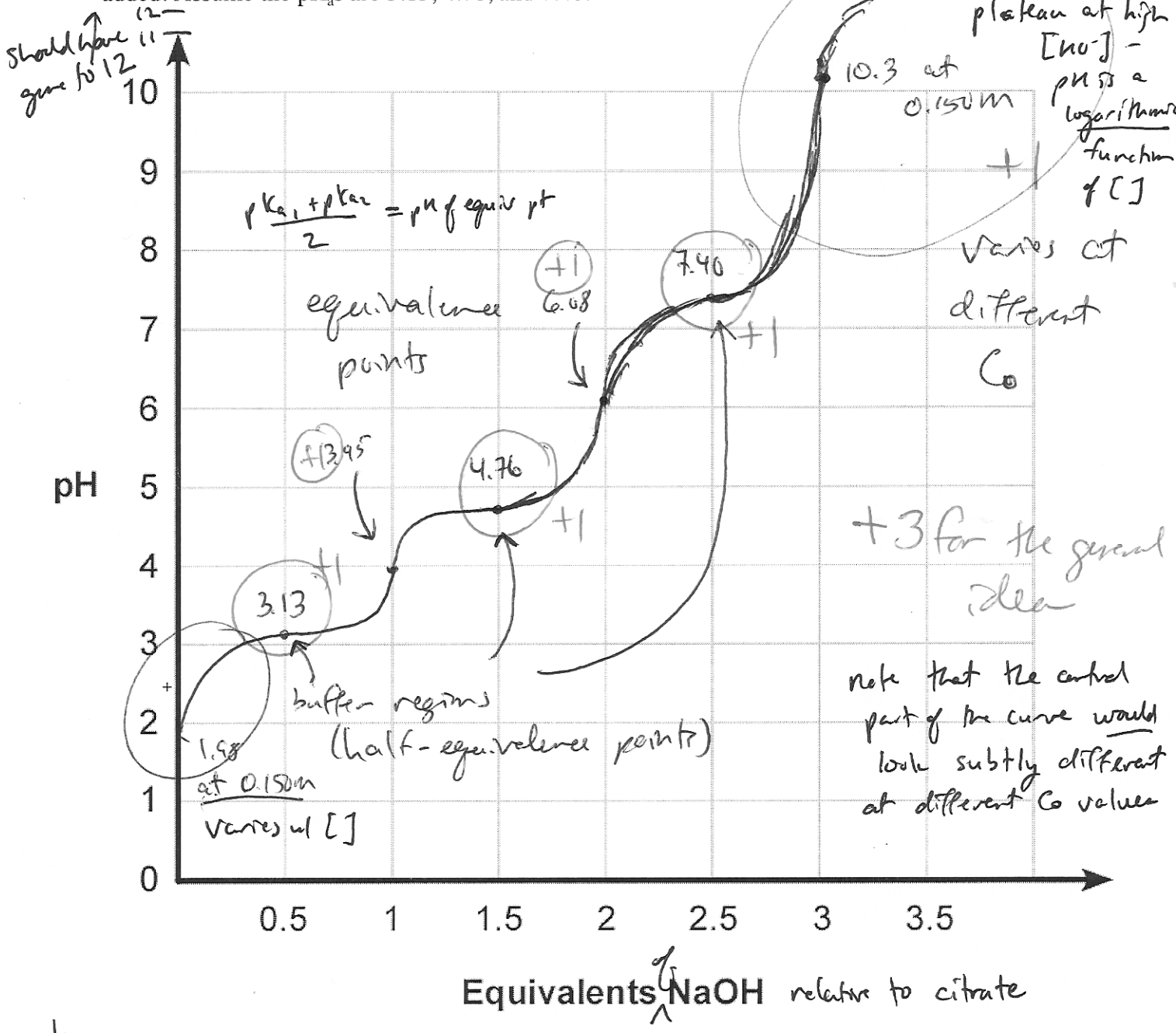
+3 for either

At 1.5×10^{-6} M, citrate can't provide enough protons to get the pH to 5.5! ($10^{-5.5}$ M = 3.16×10^{-6})

Or – Dilution drives Ka equilibrium to the right, so [HA] ↓ and [A^-] ↑.

Score for the page_____

(g; 9 pts) On the graph below, sketch the titration curve for NaOH addition to citric acid. Label the buffering regions and the equivalence points. Indicate the pH's of the centers of the buffering regions, but don't worry about the exact pH's at equivalence points. Indicate the parts of the curve that would be different depending on the actual concentration of citric acid rather than just the number of NaOH equivalents added. Assume the pK_as are 3.13, 4.76, and 7.40.



(h; 3 pts) Why is the actual last pK_a (5.40) for citrate higher than the pK_a for acetic acid (4.74)?

At that point we are deprotonating an anion – harder to remove the last proton +3

Score for the page_____

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3. (18 pts) An ideal gas, maybe.

The hydrogen economy has been proposed as a possible future solution to political and technological problems.

(a; 6 pts) What reaction is used to get useful energy from hydrogen? Why is H_2 viewed as a desirable fuel for cars, especially in urban areas?

+3 $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ [+1 for syngas rxn]

Combustion of H_2 gives only H_2O - no air pollution, "burns cleanly"

+3 or no CO_2 production

$CO + H_2O \rightarrow CO_2 + H_2$

↳ via syngas $C + H_2O \rightarrow CO + H_2$

(b; 6 pts) Why would some US policymakers love to have an efficient method of producing H_2 from coal? Explain why such a process, in and of itself, either would or would not help at all with global climate change caused by anthropogenic CO_2.

- We have a lot of coal - would be nice to use it, to

+3 free us from dependence on Mideast oil.

- If we use coal, the CO_2 goes into the atmosphere

+3 just as if we burned it. If we could sequester the CO_2 then we might really have something!

(c; 7 pts) If a car has a 50 L hydrogen fuel tank that holds H_2 gas at 200 atm pressure (roughly the pressure found in a scuba tank), at 25°C, how many grams of hydrogen are in the tank? What would be the pressure be if the same amount of hydrogen were allowed to occupy a 75 L tank?

+2 $PV = nRT$

$200 \text{ atm} \cdot 50 \text{ L} = n \cdot 0.08206 \text{ L·atm/mole K} \cdot 298.15$

$n = \frac{10000}{0.08206 \times 298.15}$ moles $= 409$ moles +1

$\times 2$ g/mole H_2 (2.016) $= 816$ g +2 (or +5 if correct)

or 826 ✓

$P_1V_1 = P_2V_2$ so $P = 200 \cdot \frac{50}{75} = 133$ atm +2

Score for the page_____

4. Fundamentals of equilibrium.

(a; 4 pts) State LeChatelier's Principle.

When a stress is applied to a reaction at equilibrium, +1 +1

the equilibrium shifts to relieve the stress. +1 +2

Consider our favorite reactions A + B <-> C, with $K_{eq} = K_1$, and C + D <-> E, with $K_{eq} = K_2$.

(b; 3 pts) In terms of K_1 and K_2, what is the equilibrium constant for C <-> B + A ?

K_{eq} for $C \rightleftharpoons B + A$ is $1/K_1$ +3

(c; 9 pts) Prove that the equilibrium constant for A + B + D <-> E is $K_1 * K_2$.

$A + B \rightleftharpoons C \quad K_1 = \frac{[C]}{[A][B]}$

$C + D \rightleftharpoons E \quad K_2 = \frac{[E]}{[C][D]}$

$A + B + D \rightleftharpoons E \quad ? K = \frac{[E]}{[A][B][D]} = K_1 \times K_2$ ✓

+3 for idea of adding reactions

+3 for writing out K_{eq}'s

+3 for $K = K_1 K_2$

Page	Score
1	/3
2	/20
3	~~/18~~ /19
4	/15
5	/12
6	/19
7	/16
Total	/104

Score for the page_____