Chemistry 271 – 23XX
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University of Maryland, College Park
General Chemistry and Energetics
Exam II (100 points)

Your Name: Key

Your SID #:

Your Section # or time:

April 6, 2016

You have 53 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.

N = 68
+2
+2

Useful Equations:

$K_a = [H^+][A^-]/[HA]$

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

$K_b = [BH^+][HO^-]/[B]$

$R = 0.08206$ L·atm/mole K

$k_B = 1.38 \times 10^{-23}$ J/K

$\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$

$K_a \times K_b = K_w$

$°C = °K - 273.15$

$P(v)dv = Cv^2 exp(-mv^2/2kT)$

$\ln k = (-E_a/RT) + \ln A$

$pH = pKa + \log([A^-]/[HA])$

$K_p = K_c(RT)^{\Delta n}$

$K_w = [H^+][OH^-] = 10^{-14}$

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. Straightforward Acid-Base (30 pts)

The equation for the dissociation of benzoic acid in water is

$$PhCOOH \rightleftharpoons H^+ + PhCOO^- \qquad K_a = 6.25 \times 10^{-5}$$

(a; 3 pts) Calculate the pKa of benzoic acid.

(+2)

$$\underbrace{pK_a = -\log(K_a)}_{(+1)} = -\log(6.25\times10^{-5}) = \underline{4.204}$$ (3 sig figs)

[+2 total for 4.2 or 4.20 and no deductions below]

(b; 9 pts) Calculate the pH of a 0.150 M solution of benzoic acid in water, assuming $x \ll C_0$. Explain or demonstrate why the $x \ll C_0$ condition is *not* satisfied for a 0.000015 M solution of benzoic acid.

ICE table:

	PhCOOH	$PhCOO^-$	H^+
I	0.150 M	0	0
C	$-x$	$+x$	$+x$
E	$0.150-x$	x	x

$$\underbrace{K_a = 6.25\times10^{-5} = \frac{x \cdot x}{0.150 - x} \approx \frac{x^2}{0.150}}_{(+3)\ \text{"}C_0\text{"}}$$

$$x = \sqrt{6.25\times10^{-5} \times 0.150} = 3.0619\times10^{-3}$$

$$pH = -\log(x) = 2.514$$ (+3)

$[x \sim 2\%$ of ~~C~~ C_0 ✓]

(+3) At $C_0 = 1.5\times10^{-5}$ M, the extent of dissociation is much larger by Le Chatelier, so x is not negligible w.r.t. C_0. And/or: $x = \sqrt{K_a C_0}$ gives $3\times10^{-3} \cdot 10^{-2} = 3\times10^{-5} > C_0$! impossible

varying explanations

(c; 4 pts) We could use benzoic acid/sodium benzoate as a buffer. Over what range of pH would such a buffer system be useful, and why?

(+2) – a $PhCOOH/PhCOO^-$ buffer would be useful over a range of ±2 (or ±1.5, or ±1) pH units away from the pKa, so between about ~~2~~ pH 2.2 – pH 6.2 (or 2.7–5.7 or 3.2–5.2)

(+2) – Outside this range ~~for~~ either [PhCOOH] or $[PhCOO^-]$ is so small that it will change markedly upon addition of acid or base – or just say that the H-H is true but not useful.

not usually mentioned.

Score for the page 16

(d; 6 pts) Write down the base dissociation equilibrium reaction and the equilibrium constant expression for benzoate ($PhCOO^-$, = the conjugate base of benzoic acid). Calculate the pKb for benzoate.

(+2) $PhCOO^\ominus + H_2O \rightleftharpoons PhCOOH + HO^\ominus$

(+2) $$K_b = \frac{[PhCOOH][HO^\ominus]}{[PhCOO^\ominus]}$$

$$K_b = \frac{K_w}{K_a} \text{ so } pK_b = 14 - pK_a = 14.-4.204$$

$$= \underline{9.796}$$ (+2)

$$\left(K_a = \frac{10^{-14}}{6.25\times10^{-5}} = 1.60\times10^{-10} \right)$$

(e; 8 pts) Calculate the pH of 0.100 M Na^+PhCOO^- (the pH you would get by dissolving 0.1 moles of sodium benzoate in 1 L of water). How did you know before you started that the answer must be > 7?

[using a consistent wrong pKb from above. is fine]

$$K_b = 10^{-9.796} = \frac{[PhCOOH][H^+]}{[PhCOO^-]} = \frac{x^2}{0.100 - x}$$ (+3)

$$x \approx \sqrt{10^{-9.796} \cdot 0.100} = \sqrt{16\times10^{-12}} = 4\times10^{-6} = [HO^-] \ll C_0 \checkmark$$

So $pH = 14 - pOH = 14 - 5.398 = \underline{8.602}$ (+3)

Sodium benzoate is the salt of a weak acid (PhCOOH) and a (+2) strong base (NaOH), therefore a solution of $NaPhCOO^-$ should be basic.

not specifically mentioned

Score for the page /14

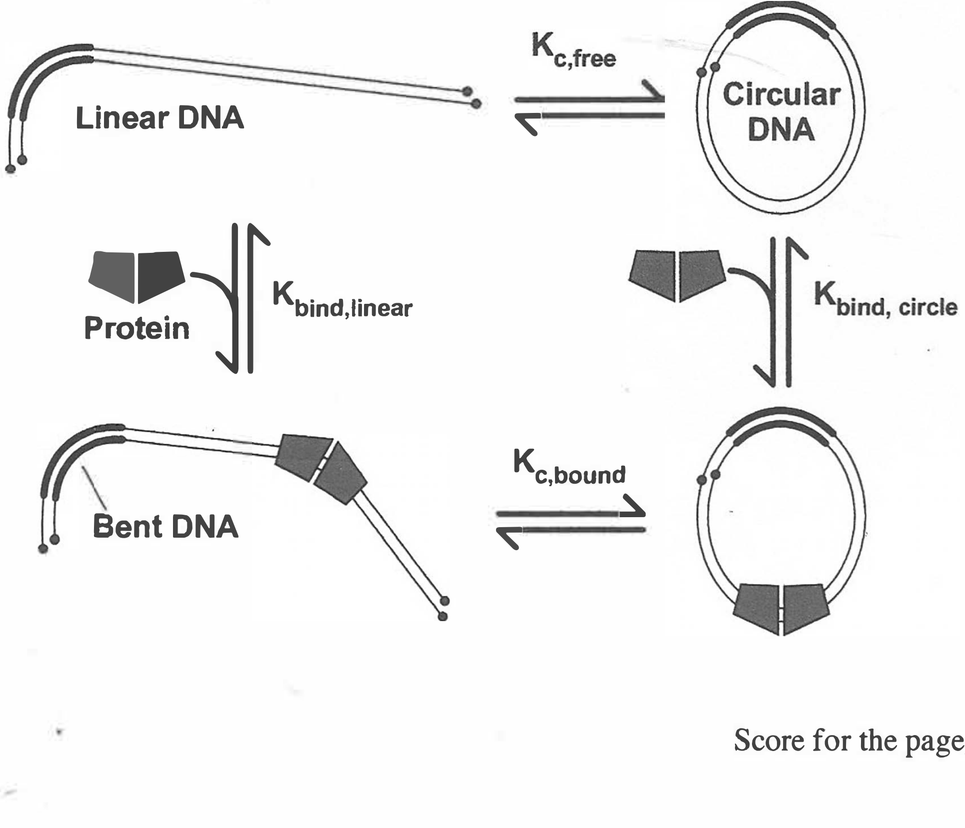
2. Linkage and Equilibria (30 pts)

(a: 10 pts) We described in class that protonation of hemoglobin is linked to the interconversion of R and T states. The R state binds O_2 much more tightly than the T state. What acid is generated by aerobic metabolism? Which state of hemoglobin is favored at acidic pH? Why is this important for mammalian physiology?

- Aerobic metabolism generates CO_2, which dissolves to give carbonic acid H_2CO_3. ((+3) for any). [Lactic acid: (+1)]
- The T state is favored in acidic conditions (the Bohr effect). (+3)
- This means that actively working muscles or tissues have lower pH, and that induces Hb to shift into the (+2) T state, which causes Hb to drop off more O_2 in those tissues. (+2)

*

The DNA double helix can bend to form small circles (hundreds of base pairs), and the circles are readily distinguishable from linear DNA. The diagram below illustrates equilibria between linear DNA on the left and circular DNA on the right. Transcription factors are proteins that bind to DNA, and in some cases they induce DNA bending, as shown for the double-quadrilateral protein. The equilibria for protein binding to linear or circular DNA are shown running vertically, with free DNA at the top and bound at the bottom. Finally, the bold lines indicate a stretch of DNA that is permanently, intrinsically curved.



Score for the page /10

(b; 8 pts) It has been found experimentally for some systems that $K_{c,bound}$ is 200× larger than $K_{c,free}$. Write down the mathematical relationship among the four equilibrium constants in the diagram. What is the value of $K_{bind,circle} / K_{bind,linear}$? Explain the linkage in words.

(+3) $\underline{K_{c,free} \cdot K_{bind,circle} = K_{bind,linear} \cdot K_{c,bound}}$ by linkage

(+1 for any linkage relationship)

(+2) So $\dfrac{K_{bind,circle}}{K_{bind,linear}} = \dfrac{K_{c,bound}}{K_{c,free}} = \underline{200}$ (just the # OK if they have some equation somewhere, otherwise +1)

(+3) The TF induces a conformational change that stabilizes the ~~[illegible]~~ ring-closed form of the DNA, and linkage tells us that therefore the TF must bind ~~[illegible]~~ more tightly to the ring-closed product of the cyclization reaction. Organic chemists call this preorganization.

(many possible answers)

(c; 12 pts) From Gilbert Problem 15.90. The equilibrium constant K_p of the reaction

$$2\ SO_3\ (g) \rightleftharpoons 2\ SO_2\ (g) + O_2\ (g)$$

is 7.69 at 830 °C. A vessel at this temperature initially contains pure SO_3 and the partial pressure of SO_3 at equilibrium is 0.100 atm. Set up the cubic equation that would give the partial pressure of O_2 at equilibrium. How would you solve the equation? Also, what is the numerical value of K_c?

ICE:

	SO_3	SO_2	O_2
I	$y \xrightarrow{\text{not}}$ 0.100!	0	0
C	$-2x$	$+2x$	$+x$
E	$y-2x$	$2x$	x

all in atm

But $y - 2x = 0.100$ – y is irrelevant!

$$K_p = \underset{(\text{atm})}{7.69} = \frac{(2x)^2(x)}{(0.100)^2_{\text{atm}}}$$ (+3)

$\underline{4x^3 = 0.0769}$ (+2)

+3 for setting I = 0.100 ~~[illegible]~~ for SO_3

$(x = 0.268\ \text{atm})$ $y = 0.636$ atm

Well, I would solve this w/ the cube root function ~~of~~ on my calculator. But OK to answer Matlab, Wolfram alpha, successive approximation, etc., esp. if you made the same mistake I did the first time and came up w/ a complicated cubic eqn. ~~(+3)~~ (+2)

$$K_c = \underbrace{\frac{K_p}{(RT)^{\Delta n}}}_{+2} = \frac{7.69\ (\text{atm})}{\left(0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \cdot 1103.15\ \text{K}\right)^{1}} = \underbrace{0.0849\ (\text{M})}_{+2}$$

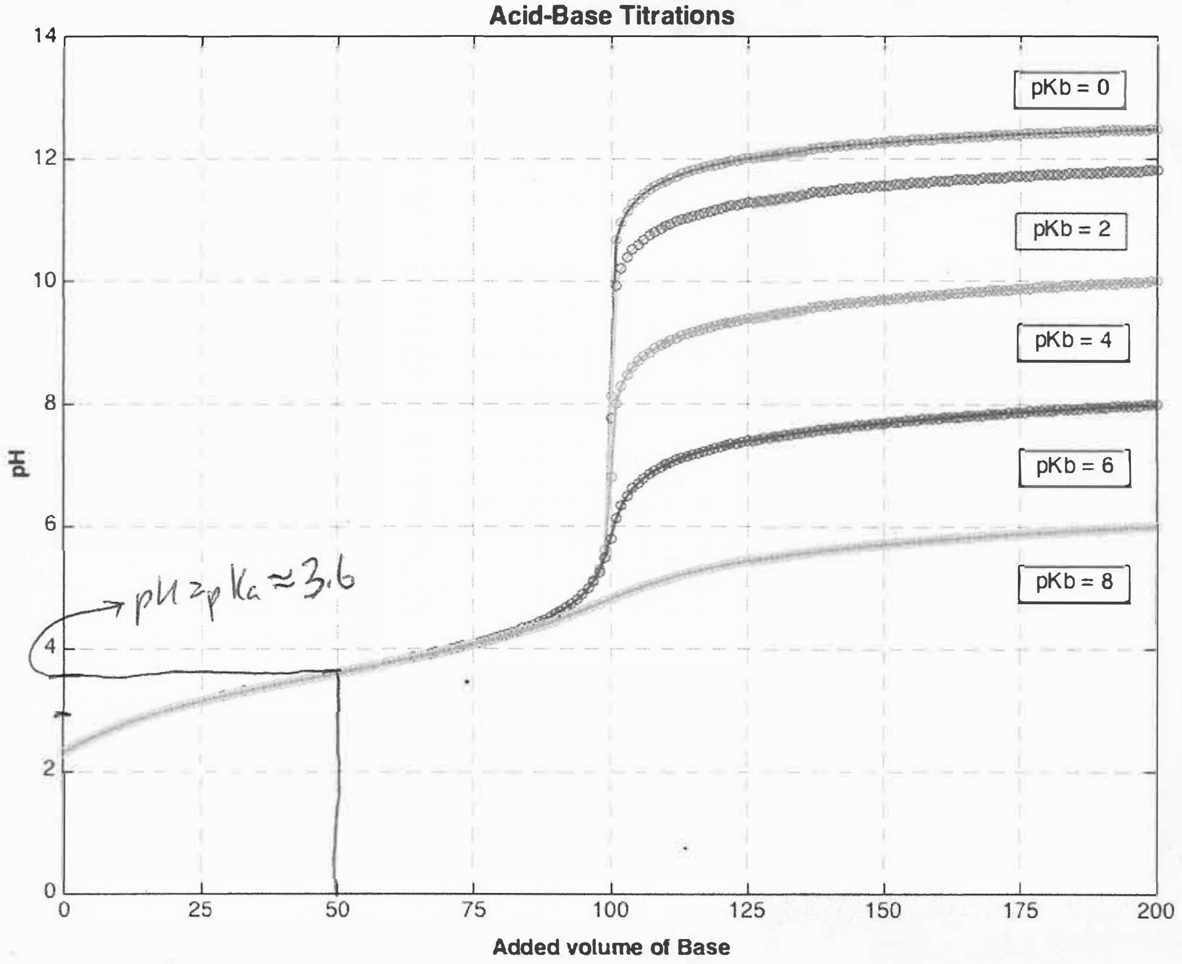
(+1) (exponent 1)

not needed (M)

$830 + 273.15 = 1103.15$

Score for the page 12/12

3. Titrations and Amino Acids (40 pts)



(a; 9 pts) The graphs above show five titrations of the same weak acid, at the same concentration, using bases with pKb's of 0, 2, 4, 6, and 8, all at the same concentration. Explain why the five curves all coincide on the left and diverge on the right. Estimate the pKa of the weak acid.

– On the left; the added base neutralizes the weak acid. Even for weak acids and bases, this reaction proceeds nearly to completion, so the identity of the base does not matter – it is just giving us A^-.

(+3)

– On the right, all of the HA is titrated so added base reacts with water, to an ~~so~~ extent dictated by the strength of the base, so stronger base gives higher pH

(+3)

– The pKa of the weak acid is about 3.6. (3.4–3.8 OK)

(+3)

Score for the page /9

(b; 9 pts) Consider the right hand edge of the graph, where 2 equivalents of base have been added. What is the ratio of $[BH^+]/[B]$ at this point for titration with a weak base? Derive the relationship apparent from the graph that pH = 14 – pKb at this point, for weak bases. In class we sometimes described the titration curve after the equivalence point as "adding base to salt." This is accurate only for titration with a strong base, for which the final pH is the same as the pH of 100 ml of base diluted to 200 ml. Qualitatively explain why is this not true as for weak bases: the pH at the end is less than the pH of pure diluted base.

- Half the added base reacted to give $A^- + BH^+$. The other half of B mostly still B for a weak base, so $\underline{([BH^+]/[B]) = 1}$ (+3)
- If we consider the HH for the acid $[BH^+]$, we have (+3)

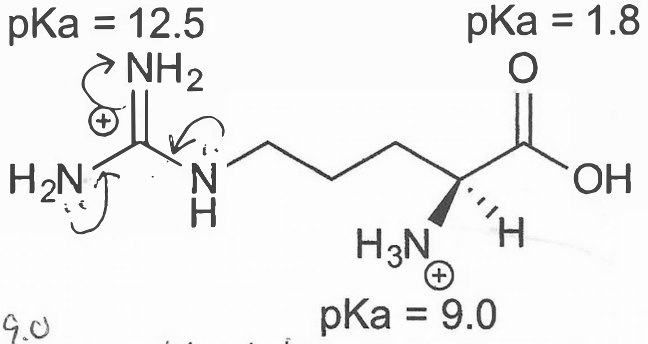
$pH = pKa + \log [BH^+]/[B] = pKa$, but the ~~K~~ $pK_a = 14 - pK_b$

so $pH = 14 - pK_b$. ✓

- For weak bases, the existing $[BH^+]$ suppresses further reaction w/ H_2O, ↓ pH vs. just dilution base (+3)

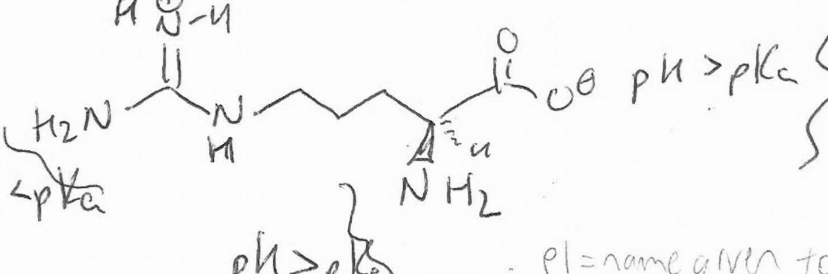
more space! ↓

(e; 10 pts) The structure of fully-protonated arginine is shown below. Draw the predominant ionic form at pH 10.75. What is the special name/symbol we give to this particular pH, for Arg? Why is the pKa for the guanidino group at the left so much higher than the pKa for the protonated amine group?



$$10.75 = \frac{12.5 + 9.0}{2} = \text{pH at the 2nd equivalence point}$$

Dominant form =



pH > pKa (+4)

Net charge = 0 so 10.75 is the $\underline{pI}$ (+3)

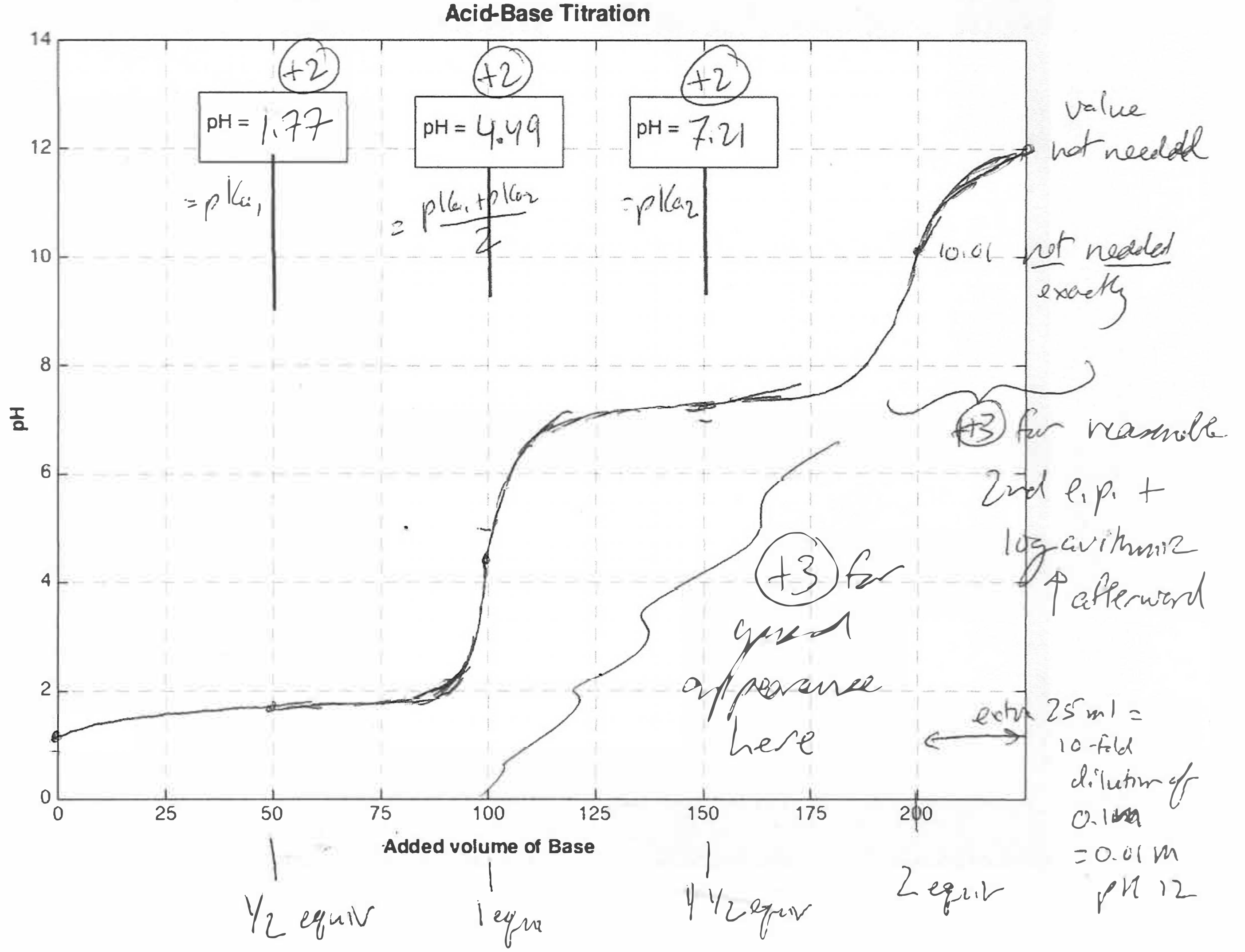
pI = name given to pH

zwitterion = form = +2

The guanidine group is a very weak acid because the ⊕ charge is delocalized by resonance. (+3)

Score for the page /19

(c; 12 pts) Sketch a titration curve for titrating 100 ml of 0.1 M sulfurous acid, H_2SO_3 with 0.1 M NaOH. The first pKa of H_2SO_3 is 1.77 and the second is 7.21. The initial pH is 1.34. Write in the pH values at the three indicated volumes of NaOH.



$\frac{1.77 + 7.21}{2} = \frac{8.98}{2} = 4.49$

2nd eq. pt is at $[OH^-] \approx \sqrt{K_b \cdot C_0} = \sqrt{\frac{10^{-14}}{10^{-7.21}} \cdot 0.1} = \sqrt{10^{-7.79}}$

$= 10^{-3.89}$

$pOH = 3.89$

$pH = 14 - 3.89 = 10.105$

not needed

Score for the page ____ /12

Page	Score	
2	~~/21~~	16
3	~~/20~~	14
4	~~/12~~	10
5	~~/18~~	/20
6	~~/17~~	9
7	~~/12~~	19
8	~~/10~~	12
Total	**/100**	100 ✓

Score for the page____________