Show all work for partial credit

1. (10 points) Calculate the pH of the following solutions:
   
   **.045M HCl**
   
   \[ [H^+] = 0.045, \text{pH} = -\log(0.045) = 1.35 \]

   **.00045 M Ca(OH)₂**
   
   \[ [\text{OH}^-] = 0.0009, \text{pOH} = -\log(0.0009) = \text{pOH} = 3.046; \text{pH} = 14 - 3.046 = 10.95 \]

   **.00000045M HNO₃**
   
   While it isn’t as obvious in this problems as in some others, because the H⁺ is only \(4.5 \times 10^{-7}\), you have to consider the \(1 \times 10^{-7}\) H⁺ from the autoionization of water to get correct answer here.

   If you ignore the autoionization you get \(\text{pH} = -\log(4.5 \times 10^{-7}) = 6.35\)

   If you do the quick and dirty approach, where you add the H⁺ from water to the H⁺ from the acid you get \(\text{pH} = -\log(1 \times 10^{-7} + 4.5 \times 10^{-7}) = 6.26\) which looks pretty significant.

   If you do it right, as I show you in the next chapter that was not covered in this test, then you get to the equation \(K_w = 1 \times 10^{-14} = X(4.5 \times 10^{-7} + X)\), and \(X = [\text{OH}^-]\), solving for \(X\) you get that \([\text{OH}^-] = 2.12 \times 10^{-8}\) and \([\text{H}^+] = 4.72 \times 10^{-7}\) so \(\text{pH} = 6.32\), and you see that the quick and dirty answer was actually a bit off.

2. (10 points) The small and taste of fish arises from amine compounds. Suggest a reason why adding lemon juice (which is acidic) reduces the ‘fishy’ smell. Suggest another common household product you use to reduce the fishy smell if you didn’t have lemon juice.

   Amines in the protonated form are going to have a charge, and with the charge they are going to want to stay in the aqueous phase where the water molecules will surround the charge. On the other hand, in the deprotonated form, the molecule has no charge and therefore is not very soluble, and in fact, will prefer to go into the gas phase to get away from the water. Thus the protonated forms will be water soluble and have little smell, but the deprotonated form will not be water soluble, but will prefer to be a gas, so they will smell. Since the acid of lemon juice will tend to protonate the amines, this will push these compounds into the water soluble, non-smelly form, so your fish smells less, so it will taste less fishy. Any acid will do this, and the other common acid I was looking for was vinegar. Several people didn’t like the idea of putting vinegar on fish, but this is actually a standard condiment at Fish and Chips restaurants. Look for it next time you are at Long John Silver’s!
3. (10 points) I have an acid solution that has a formal concentration of .001M; at this concentration the acid is 7.5% dissociated. What is the pH of the solution, and what is the pKa of the acid?

\[
\frac{[A^-]}{[HA] + [A^-]} \times 100\% = 7.5\%
\]

\[
.001M = [HA] + [A^-]
\]

\[
\frac{[A^-]}{.001 \times 100\%} = 7.5\%; \quad [A^-] = .001(7.5\%)/100\% = 7.5 \times 10^{-5}
\]

if \([A^-] = 7.5 \times 10^{-5}\), then \([H^+] = 7.5 \times 10^{-5}\), and \(\text{pH} = 4.12\)

The K is then \(K = (7.5 \times 10^{-5})^2/0.001-7.5 \times 10^{-5}) = 6.08 \times 10^{-6}\); \(\text{pKa} = 5.22\)

4. (10 points) Butanoic acid (CH₃CH₂CH₂COOH) is a weak acid with a pKa of 4.818. What is the pH of a 0.02M solution of Sodium butanate (CH₃CH₂CH₂COONa)?

While I give you an acid here, what I am asking for is the pH of the conjugate base form, so this is the pH of a weak base problem

\(K_B = K_w/K_A\), or \(pK_B = 14-pK_a = 9.182\); \(K_B = 10^{-9.182} = 6.58 \times 10^{-10}\)

The reaction is:

\[\text{But}^- + \text{H}_2\text{O} \rightleftharpoons \text{HBut} + \text{OH}^-\]

\(K_B = [\text{HBut}][\text{OH}^-]/[\text{But}^-]\)

\(6.58 \times 10^{-10} = X^2/(0.02-X)\), where \(X = [\text{OH}^-] = [\text{HBut}]\)

I will assume that since \(K\) is very small that I can assume that \(0.02-X \approx 0.02\)

\(6.58 \times 10^{-10} \times 0.02 = X^2\)

\(X = 3.63 \times 10^{-6}\); \(\text{pOH} = 5.44\), \(\text{pH} = 14-5.44 = 8.56\)
5. (10 points) I want to make a buffer that will keep the pH of a solution at 11.0. If I start by dissolving 15 g of piperidine in 1L of water, how many mls of either 1M HCl, or 1M NaOH will I have to add to this solution to make my buffer?

\[
\begin{align*}
\text{Piperidine, } \text{pKa}=11.125
\end{align*}
\]

From the above structure you should come up with the formula C_5H_11N for piperidine, and get a molar mass of 85.148 g

We then have 15/85.148 or .176 moles of pip to play with. Piperidine refers to the free base, or fully deprotonated form shown above, so we will have to add acid change the Pip into the protonate PipH^+ to get a buffer mixture of base and conjugate acid.

Fortunately the HH equation applies to either bases or acids, the only thing you have to do is keep the HA an and A^- (protonated and deprotonated) forms straight

\[
\text{pH} = \text{pKa} + \log \frac{A^-}{HA} ; \text{pH} = \text{pKa} + \log \left(\frac{\text{deprotonated}}{\text{protonated}}\right) ; \text{pH} = \text{pKa} + \log(\text{Pip}/\text{HPip})
\]

Since we are starting with Pip, Pip in this equation will be .176-X, and HPip = X = amount of H added

\[
11.0 = 11.125 + \log \frac{.176-X}{X}
\]

\[-.125 = \log \frac{.176-X}{X}
\]

\[10^{-125} = \frac{.176-X}{X} ; .75 = \frac{.176-X}{X} ; .75X = .176-X ; .176 = 1.75X, X = .10\text{moles}
\]

So I need to add .1 moles of HCl to the solution 1M = .1/l of HCl; I need 100 mls of HCl

Several people assumed that they started with the HPip form and added base to make the buffer. While this is technically not the correct form to start with, I allowed this solution as long as you did the math right.

6. (10 points) Piperazine has the structure shown below, and has 2 pKa , 5.3 and 9.7. Make a rough sketch of the titration curve you would expect to see if you titrated 10 mls of a 0.1M solution of Piperazine with .05 M HCl. (Hint: Emphasis on rough, do not use you calculator for this problem)

\[
\begin{align*}
\text{HN} & \quad \text{HN}
\end{align*}
\]
Take Home Portion

Now let's do that last problem more exactly.

1A. (20 points) Piperazine has the structure shown below, and has 2 pK’a, 5.333 and 9.731. Calculate the titration curve you would get if you titrated 10 ml of a 0.1M solution of Piperazine with .05 M HCl. On this titration curve calculate the pH of the solution at the following points: Initial, 1/4 way to the 1st equivalence point, the 1st equivalence point, 3/4 of the way between the 1st and 2nd equivalence points, the 2nd equivalence point, and 5 ml past the 2nd equivalence point.

\[
\text{P Piperazine structure}
\]

1A Initial pH (4 points)
- treat as weak base

\[
K_b = K_w / K_a
\]
\[
K_a = 10^{-9.731} = 1.86 \times 10^{-10}
\]
\[
K_b = 1 \times 10^{-14} / 1.86 \times 10^{-10} = 5.38 \times 10^{-5}
\]
\[
K_b = \left[ \frac{[OH^-][BH^+]}{[B]} \right]; [B] = 0.1, X = [OH^-] = [BH^+] = 5.38 \times 10^{-5}
\]
\[
X = \frac{[OH^-]}{2.29 \times 10^{-3}}; pOH = 2.64, pH = 11.36
\]

1/4 of way to 1st equivalence point (4 points)
1st equivalence point is where mole base = moles acid
Mole base = M\times V = 0.1 \times 0.01 = .001
Mole acid = .001 = M\times V = .05(X); X = .001/.05 = .02l = 20 ml
so 1/4 of way is at 5 ml of acid
Acid-base reaction is: H⁺ + Pip ^ → HPip⁺
Here have .001 moles Pip, .005\times .05 = .00025 mole H⁺
\[
\text{Pip = .001-.00025 = .00075}
\]
\[
\text{HPip⁺ = .00025}
\]

Using H H equation:
\[
pH = pK_a + \log \frac{[A^-]}{[HA]} \text{ but recognizing that } [A^-] = \text{Pip} \text{ and } [HA] = \text{HPip⁺}
\]
\[
pH = pK_a + \log \frac{\text{Pip}}{\text{HPip⁺}}
\]
\[
pH = 9.731 + \log \left( \frac{.00075}{.00025} \right) = 10.21
\]

1st equivalence point (4 points)
Quick and Dirty, pH = (pK₁+pK₂)/2 = 7.53
Just to check if assumptions to use this equation are true
Is $K_1K_w \ll K_1K_2F$?
$F = .01(.1)/(.01+.02) = .003333$
$K_i = 10^{-5.333} = 4.64 \times 10^{-6}$
$K_1K_w = 4.64 \times 10^{-6} \times 1 \times 10^{-14} = 4.64 \times 10^{-20}$
$K_1K_2F = 4.64 \times 10^{-6} \times 1.83 \times 10^{-10} \times .003333 = 2.83 \times 10^{-18}$
YES

Is $K_1 \ll F$
$4.64 \times 10^{-6} \ll .003333$
Yes

So the quick and Dirty equation is good

3/4 of way between 1st and 2nd equivalence points (4 points)
If first EQ pt is 20, then the second must be at 40
so 3/4 of the way between 20 and 40 is at 35 mls

At 35 mls have added $0.035 \times 0.05 = 1.75 \times 10^{-3}$ moles of acid
At start had $0.1 \times 0.01 = 0.001$ moles of Pip
used $0.001$ moles of acid to change Pip to HPip$^+$
Now only have 0.0075 moles of Acid left and this reacts with HPip$^+$
HPip$^+$ = HPip$^+$ - Acid = 0.001 - 0.0075 = 0.0025
H$_2$Pip$^{2+}$ = moles acid = 0.0075

Again in a buffer so can use HH, but let’s make the HH look like this system

\[
\text{pH} = pK_a + \log \left( \frac{A^-}{HA} \right) = pK_a + \log \frac{[HPip^+]}{[H_2Pip^{2+}]} \\
\text{pH} = 5.333 + \log (0.0025/0.00075) \\
\text{pH} = 4.86
\]

2nd equivalence point
At this point the base has been turned into its fully protonated conjugate acid, so you calculate the pH as you would for any weak acid.

\[
[HA] = 10^{0.1}/50 = 0.02
\]

\[
K_a = \frac{[H^+][A^-]}{[HA]}
\]

\[
4.64 \times 10^{-6} = \frac{X^2}{0.02 - X}
\]

Solving with Quadratic

\[
X = 3.025 \times 10^{-4}; pH = 3.52
\]
5 ml past 2\textsuperscript{nd} equivalence point (4 points)

This is pH base on excess acid

excess acid is (.005L \times .05)

Total volume is now 10 + 45 ml

\[ [H^+] = \frac{(0.005 \times 0.05)}{0.055} = 4.545 \times 10^{-3} \text{ M}; \text{pH} = 2.34 \]

1B. (10 points) Based on the equivalence points you calculated 1A, and the table of indicators found in your text, what is the indicator you should use to find your 1\textsuperscript{st} equivalence point? Your 2\textsuperscript{nd} equivalence point?

1\textsuperscript{st} equivalence point is at pH 7.53, Neutral Red (7.41)

2\textsuperscript{nd} equivalence point is at pH 3.52, Methyl Orange (3.75)

1C. (10 points) Based on the titration curve you calculated in 1A; tell me the principal species of Piperazine present at the following pH’s: 7, 8, 9, 10, 11, 12. At what pH will the principal species have a net +2 charge? A net +1 charge? A 0 net charge. A net -1 charge? A net -2 charge?

Pip will be the dominant form until pH<9.731 (pKa) Will then be in HPip\textsuperscript{+} form pH < 5.33 (pK\textsubscript{a1}) Is in H\textsubscript{2}Pip\textsuperscript{2+} at all pH’s lower than 5.33

Putting this into a table

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<th>pH</th>
<th>Form</th>
<th>Charge</th>
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<td>Pip</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>Pip</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Pip</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>HPip\textsuperscript{+}</td>
<td>+1</td>
</tr>
<tr>
<td>8</td>
<td>HPip\textsuperscript{+}</td>
<td>+1</td>
</tr>
<tr>
<td>7</td>
<td>HPip\textsuperscript{+}</td>
<td>+1</td>
</tr>
</tbody>
</table>

It will only have a +2 charge if the pH <=5
It never be in a negatively charged form.