Chemistry 222 Name_____
**Spring 2017** **80 Points**
Exam 3: Chapters 8-10

Complete five (5) of problems 1-6. CLEARLY mark the problem you do not want graded. Report your answers with the appropriate number of significant figures and with the appropriate units. (16 points each)

1. You need to prepare a pH 1.50 buffer by adjusting the pH of 200.0 mL of a 0.200 M solution of monosodium oxalate ($NaHC_2O_4$). The only acid and base solutions you have available are 100 mL of 0.100 M NaOH, and 100 mL of 0.100 M HCl. Given these solutions, can you make your buffer? *Justify your answer with appropriate calculations*.

   (For oxalic acid, pK_{a1} = 1.25, pK_{a2} = 4.26.)

There are two equilibria here to consider:

$$H_2C_2O_4 = H^+ + HC_2O_4^- \qquad pK_{a1} = 1.25$$
$$HC_2O_4^- = H^+ + C_2O_4^{2-} \qquad pK_{a2} = 4.26$$
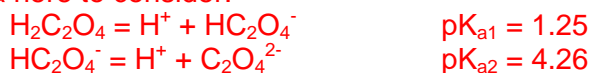
Since the desired pH of our buffer is closest to pK_{a2}, we should focus on the $HC_2O_4^-/H_2C_2O_4$ conjugate acid/base pair for our buffer. This will require the addition of HCl to convert some of the $HC_2O_4^-$ to $H_2C_2O_4$. What ratio of $HC_2O_4^-/H_2C_2O_4$ is needed?

$$pH = pK_{a2} + \log \frac{mol\ HC_2O_4^-}{mol\ H_2C_2O_4}$$

$$1.50 = 1.25 + \log \frac{mol\ HC_2O_4^-}{mol\ H_2C_2O_4^-}$$

Rearranging shows us that the ratio of mol $HC_2O_4^-$/mol $H_2C_2O_4$ must be 1.778. Do we have enough HCl to do this? How many mol HCl are needed? Initially, we have 200 mL x 0.200 M = 40.0 mmol mol $HC_2O_4^-$, so the total moles of $HC_2O_4^-$ and $H_2C_2O_4$ must be 40.0 (because of mass balance and ignoring Ka_2). So 40.0 = mol $HC_2O_4^-$ + mol $H_2C_2O_4$

$$1.778 = \frac{mol\ HC_2O_4^-}{mol\ H_2C_2O_4} = \frac{40.0 - mol\ H_2C_2O_4}{mol\ H_2C_2O_4}$$

Solving for mol $H_2C_2O_4$ tells us that we need to produce 14.4 mmol $H_2C_2O_4$ to get to our desired ratio. This requires 14.4 mmol x 1L/0.100mol = 144 mL HCl to react with $HC_2O_4^-$, but we only have 100 mL, therefore, we can't make the buffer!

Alternate Approach:
You could also calculate the maximum pH you could make given the solutions you have. If you add all 100 mL of HCl to your HA^- solution, the you will form:

	HA^-	+	H^+	$\rightarrow$	H_2A	+	H_2O
Start (mmol)	40.0		10.0		0		0
End (mmol)	30.0		0		10.0		10.0
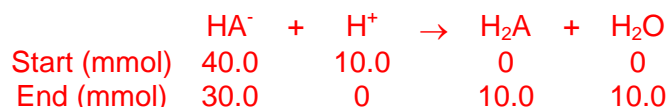
So, the pH of a solution of 30.0 mmol HA^- and 10.0 mmol H_2A will be:
$$pH = pK_{a1} + \log \frac{mol\ HA^-}{mol\ H_2A} = 1.25 + \log \frac{30.0}{10.0} = \mathbf{1.73}$$

Since this is the minimum pH we can make with these solutions, and it is higher than our target pH (1.50), we cannot make the buffer with these materials.

2. Answer the following: (8 points each)
   a. Why is the pH of a buffer effectively independent of dilution, while the capacity of the buffer diminishes as it becomes more dilute?

   The key points for discussion here are:
   • the ratio of weak acid to conjugate base stays essentially constant with dilution
   • the buffer capacity suffers as the buffer is diluted because the addition of strong acid or base will cause a larger shift in the weak acid:conjugate base ratio.

   b. Why is a buffer solution most effective at a pH within ±1 of the pK_a for the acid used to make the buffer?

   The key here is that the buffer capacity for a buffer solution is best when the ratio of A^- to HA is close to 1. This occurs when the pH = pKa. Within ±1 of the pK_a the ratio is still reasonable, between 0.1 and 10. Outside this range, there is too little of either A^- or HA to allow for reasonable buffer capacity because the addition of even a small amount of H^+ or OH^- can cause the ratio to change significantly.

3. For this problem consider the newly discovered *trumanic acid*, a triprotic weak acid of the form H_3A.

   a. The plot below represents the fraction of dissociation for trumanic acid. Label the four curves with their corresponding alphas (α_{H3A}, α_{H2A-}, α_{HA2-}, α_{A3-}) and determine the values for pK_{a1}, pK_{a2}, and pK_{a3}. (6 points)

The pK's occur where alpha lines for two protonation states cross at 0.50. Therefore:
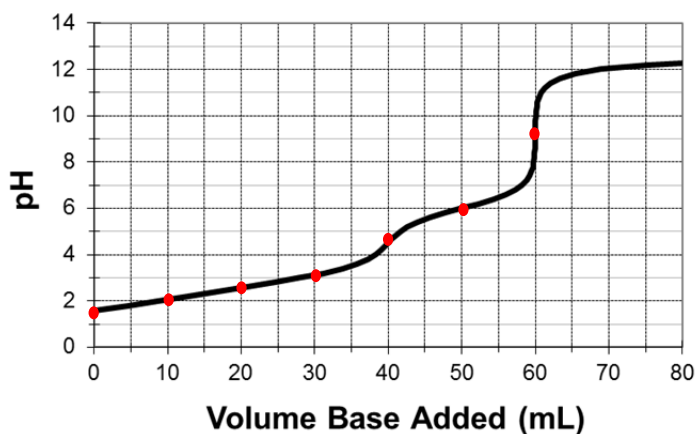**pK_{a1} = 2.00**
pK_{a2} = 3.00
pK_{a3} = 6.00
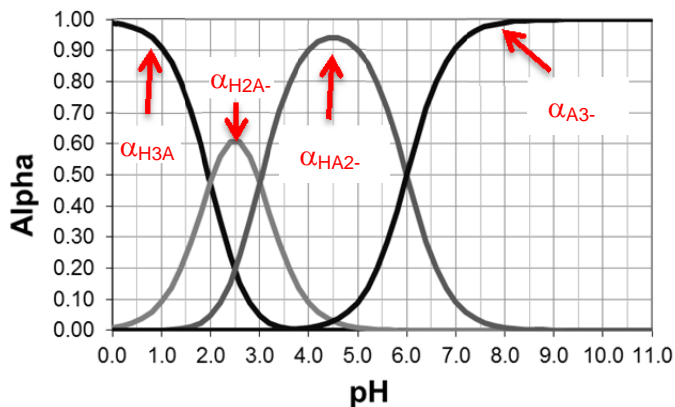
   b. Based in your results from part a, use the axes below to sketch the titration curve for the titration of 20.0 mL of a 0.100 M solution of trumanic acid with 0.100 M NaOH. Specify the pH at a minimum of five points on the plot. (10 points)

Given that the formality of our acid is the same as the NaOH, we expect equivalence points to occur at 20, 40, and 60 mL of titrant added. From our pK_a values, we can estimate the pH at the first two equivalence points because the primary species that are present are the amphiprotic forms. Midway to each equivalence point, pH is determined by pK_a's

At 20 mL, pH = $(pK_{a1}+pK_{a2})/2$ = (2.00+3.00)/2 = 2.50
At 40 mL, pH = (3.00 + 6.00)/2 = 4.50
At 10 mL, pH = pK_{a1} = 2.00
At 30 mL, pH = pK_{a2} = 3.00
At 50 mL, pH = pK_{a3} = 6.00

Other useful points would be:
- At 0 mL, the solution can be treated as a monoprotic weak acid using an ICE table. Doing so leads to a pH of 1.55.
- At the last equivalence point, we have a solution of A^{3-}, which can be treated as a monobasic weak base using an ICE table. Doing so leads to a pH of 9.20.
- At an infinite volume of base added, the pH approaches the pH of 0.10 M NaOH, pH 13.00,

Notice that the first equivalence point is not very sharp. This is also evidenced in the alpha plots in that α_{H2A-} never gets close to 1.

4. Complete the following: (8 points each)
   a. Calculate the pH of a 4.5×10^{-8} F solution of HCl.

   Although HCl is a strong acid, the concentration is low enough that we need to consider the contribution of water as a source of H^+. Start by writing mass and charge balance equations:

   $$\text{Charge Balance: } [H^+] = [Cl^-] + [OH^-]$$
   $$\text{Mass Balance: } [Cl^-] = 4.5 \times 10^{-8}\, M$$

   Substituting the mass balance expression in to the charge balance and using K_w, we can get everything in terms of $[H^+]$:

   $$[H^+] = 4.5 \times 10^{-8} + K_w/[H^+] \rightarrow\rightarrow [H^+]^2 - 4.5 \times 10^{-8}[H^+] - K_w = 0$$

   Solving the quadratic gives $[H^+] = 1.25 \times 10^{-7}\, M$ or **pH = 6.90**

   b. A 0.020 F solution of phthalic acid ($pK_{a1} = 2.95$, $pK_{a2} = 5.41$) is buffered at pH 4.50. What fraction of the phthalic acid is present as the amphiprotic form at this pH?

   $$\alpha_{HA^-} = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$
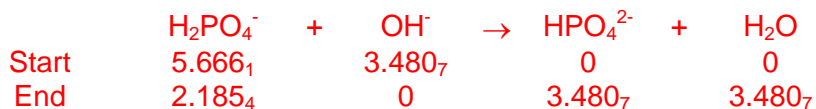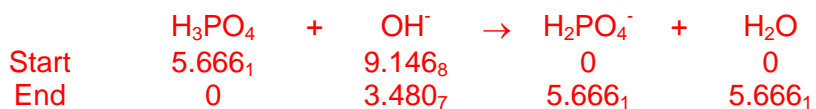
   With $[H^+] = 3.162 \times 10^{-5}\, M$, $K_{a1} = 10^{-2.95} = 1.12 \times 10^{-3}$, and $K_{a2} = 10^{-5.41} = 3.89 \times 10^{-6}$;
   $\alpha_{HA^-} = 0.869$, or 87% is present as HA^-.

5. What is the pH of a solution prepared by adding 52.00 mL of 0.1759 M NaOH to 51.00 mL of 0.1111 M H_3PO_4? For phosphoric acid: $K_{a1} = 7.11 \times 10^{-3}$, $K_{a2} = 6.32 \times 10^{-8}$, $K_{a3} = 4.5 \times 10^{-13}$.

mmol H_3PO_4 initial = 51.00 mL x 0.1111 mol H_3PO_4/L = 5.666_1 mmol H_3PO_4
mmol OH^- added = 52.00 mL x 0.1759 mol OH^-/L = 9.146_8 mmol OH^-

So, after reaction, all of the H_3PO_4 will have been converted to, and some will have been converted to HPO_4^{2-}. How much of each will remain?

	H_3PO_4	+	OH^-	$\rightarrow$	$H_2PO_4^-$	+	H_2O
Start	5.666_1		9.146_8		0		0
End	0		3.480_7		5.666_1		5.666_1

	$H_2PO_4^-$	+	OH^-	$\rightarrow$	HPO_4^{2-}	+	H_2O
Start	5.666_1		3.480_7		0		0
End	2.185_4		0		3.480_7		3.480_7

Using Henderson-Hasselbach eqn:

$$pH = pKa_2 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.20 + \log \frac{3.480_7}{2.185_4} = \mathbf{7.41}$$

6. A new quant. student Ty Trate is struggling to select an indicator appropriate for his titration of a 0.010 M solution of the weak base pyridine (pK_b = 8.77) with 0.010 F HCl using an appropriate indicator. Help Ty select an appropriate indicator from the list below and point out the problems that would arise if an inappropriate indicator was chosen.
(*Note: your justification and explanation is more valuable than picking the "right" indicator*)

Indicator	Transition Range
Thymol Blue	1.2-2.8
Bromocresol Green	3.8-5.4
Chlorophenol Red	4.8-6.4
Phenolphthalein	8.0-9.6

In choosing an indicator, your should select a compound who's transition range overlaps the steepest part of the titration curve, so, we need to calculate the pH at the equivalence point in order to make our selection. At the equivalence point, all of B has been converted to BH^+. If the initial pyridine concentration is ~0.01 M, the BH^+ concentration at the equivalence point will be 0.0050 M.

$BH^+ = B + H^+$, $pK_a = 14 - K_b = 5.23$, $K_a = 5.89 \times 10^{-6}$
At the equivalence point: $(x = [H^+])$

$$K_a = \frac{x^2}{0.005 - x}$$

Let's solve for x: $x = 1.69 \times 10^{-4}$ M = $[H^+]$, pH = 3.77
The indicator that most closely matches this pH is **Bromocresol Green**.

Poor choice of an indicator will lead to inaccuracy in the endpoint determination. If the indicator transition range occurs before the endpoint is reached, the value of the equivalence point will be underestimated. If the transition range of the indicator is too far past the equivalence point, the titration will be overshot.

Possibly Useful Information

$$\left[H^+\right] = \sqrt{\dfrac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$$	$$pH = \frac{1}{2}\left(pK_{a1} + pK_{a2}\right)$$
$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}$$	$$\alpha_{H_2A} = \frac{\left[H^+\right]^2}{\left[H^+\right]^2 + \left[H^+\right]K_{a1} + K_{a1}K_{a2}}$$
$$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{\left[H^+\right]^2 + \left[H^+\right]K_{a1} + K_{a1}K_{a2}}$$	$$K_aK_b = K_w$$
$$K_w = 1.0 \times 10^{14} = [H^+][OH^-]$$	$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

PERIODIC CHART OF THE ELEMENTS

FoxTrot Classics by Bill Amend