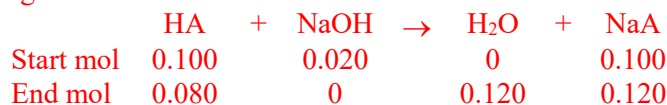**Do <u>five</u> of problems 1-6. Clearly mark the problems you do not want graded. (16 pts. ea.)** You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. You may ignore activities in all problems.

1. Find the pH of a solution prepared by dissolving all of the following compounds in water in one beaker and diluting to a volume of 0.500 L: 0.100 mol acetic acid (pK_a = 4.76), 0.100 mol sodium acetate, 0.040 mol HCl, and 0.060 mol NaOH.

We need to recognize that the strong acid and strong base will react until one is consumed:

	HCl	+	NaOH	→	NaCl	+	H_2O
Start mol	0.040		0.060		0		0
End mol	0		0.020		0.040		0.040
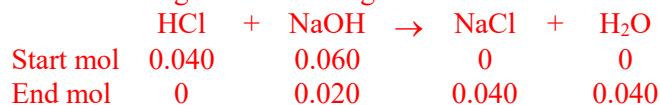
Now, the excess strong acid will react:

	HA	+	NaOH	→	H_2O	+	NaA
Start mol	0.100		0.020		0		0.100
End mol	0.080		0		0.120		0.120

So, we now have a buffer with 0.090 mol acetic acid and 0.110 moles acetate:

$$pH = pK_a + \log \frac{mol\ A^-}{mol\ HA} = 4.76 + \log \frac{0.120\ mol}{0.080\ mol} = \mathbf{4.94}$$

In the end, **pH = 4.94**

2. You are asked to prepare 0.500 L of 0.200 M acetate buffer at pH 4.90 using only pure acetic acid (MW=60.05 g/mol, pK_a=4.76), 3.00 M NaOH, and water.
   a. How many grams of acetic acid will be needed to prepare the 0.500 L buffer? Note that the given concentration of acetate refers to the concentration of all acetate species in solution. (6 points)

Regardless of pH, the total concentration of acetate must be 0.200 M. We will start with a 0.200 M acetic acid solution and use NaOH to adjust pH. Therefore, we need to solution initially to be 0.200 M acetic acid.

$$\frac{0.200 \text{ mol HA}}{1 \text{ L}} \quad \text{x} \quad 0.500 \text{ L} \quad \text{x} \quad \frac{60.05 \text{ g HA}}{1 \text{ mol HA}} \quad = \quad 6.005 = \textbf{6.01 g acetic acid}$$

   b. What volume of 3.00 M NaOH, must be added to the acetic acid to achieve a buffer with a pH of 4.90 at a final volume of 0.500 L? Ignore activity coefficients. (10 points)

We need to add enough NaOH to produce the appropriate ratio of A⁻:HA to produce pH 4.90. What ratio do we need?

$$pH \quad = \quad pK_a \quad + \quad \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$4.90 \quad = \quad 4.76 \quad + \quad \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$10^{(4.90-4.76)} \quad = \quad 1.38 \quad = \quad \frac{\text{mol A}^-}{\text{mol HA}}$$

So, 1.38(mol HA) = mol A⁻
From mass balance, we know that mol HA + mol A⁻ = (0.500L)(0.200M) = 0.100 mol

Now some algebra to find how many mol A⁻ we need to produce:

$$1.38(\text{mol HA}) = \text{mol A}^- \text{ or mol HA} = \text{mol A}^-/1.38$$
$$\text{mol HA} + \text{mol A}^- = 0.100$$
$$(\text{mol A}^-/1.38) + \text{mol A}^- = 0.100$$
$$\text{mol A}^-((1/1.38) + 1) = 0.100$$
$$\text{mol A}^- = 0.0579_8 \text{ mol}$$

To produce mol A⁻ = 0.0579_8 mol A⁻ we need to add 0.0579_8 mol NaOH. That will require:

$$0.0579_8 \text{ mol NaOH} \quad \text{x} \quad \frac{1000 \text{ mL}}{3.00 \text{ mol NaOH}} \quad = \quad \textbf{19.3 mL NaOH}$$

3. I've asked you to go into the lab and help me prepare some unknowns for a new acid/base titration experiment we are considering. Unfortunately, I have neglected to label one solution and am nowhere to be found. To identify the solution, you construct the titration curve below by titrating 20.00 mL of the acid solution with standard 0.100 M NaOH. From the titration curve and the list of possible solution compositions below, identify the composition of the solution. _Justify your reasoning by explaining how you were able to rule out each of the imposters and choose the appropriate identity_.

Solution	pK$_a$
A: 0.100 M acetic acid	4.76
B: 0.100 M maleic acid	1.83, 6.07
C: 0.100 M nicotinic acid	2.03, 4.08
D: 0.100 M succinic acid	4.21, 5.64
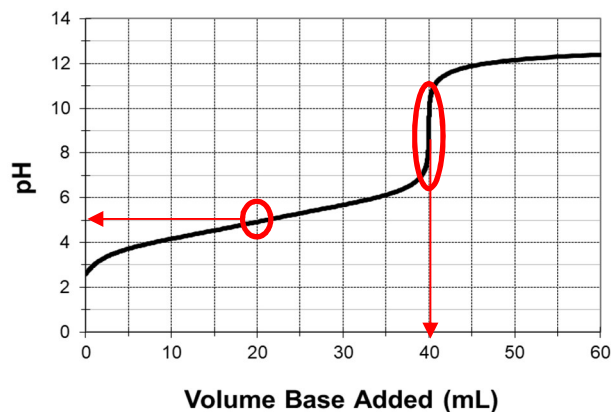
Before examining the candidates, let's take a look at the titration curve and see what it can tell us. (1) we see a single clear equivalence point, indicative of either a monoprotic weak acid or a diprotic weak acid with Ka's that are "close". The pH midway to the sharp equivalence point is ~5, which would correspond to the pKa if the acid is monoprotic or to the average of the pKa values if the acid is diprotic. (2) We see the sharp equivalence point at 40 mL titrant added. We are titrating 20.00 mL of a 0.100 M solution of our acid with 0.100 M NaOH. If the acid were monoprotic, we would expect an equivalence point at 20.00 mL. The fact that the sharp equivalence point occurs at 40 mL indicates a diprotic acid. From this information, we can assess our candidates.

A: 0.100 M acetic acid. While the pKa does correspond to the pH half way to the equivalence point, if this were the identity, our equivalence point would occur at 20 mL, not 40 mL. So the acid cannot be acetic acid.

B: 0.100 M maleic acid. Maleic acid is diprotic, but the Ka values are far enough apart that we would expect two distinct equivalence points. Maleic cannot be the unknown acid.

C: 0.100 M nicotinic acid. Nicotinic acid is diprotic and the Ka values are close to one another, so the absence of two clear equivalence points makes sense. However, the average of the pKa values is 3.05, which does not correspond to the value at 20 mL in the titration curve. So nicotinic is not the unknown acid.

D: 0.100 M succinic acid. Succinic is diprotic, with the Ka values close to one another, so the absence of two clear equivalence points is reasonable. Also, the average of the pKa values is 4.92, which corresponds to the value at 20 mL in the titration curve. **Therefore, succinic is the most likely identity for the unknown acid.**

4. Calculate the pH of 6.6×10^{-7} M nitric acid. What fraction of the total H^+ in this solution is from the nitric acid?

You **must** use charge (or mass) balance to solve this problem!

$$H_2O = H^+ + OH^-, K_w = [H^+][OH^-]$$

Charge Balance: $[H^+] = [NO_3^-] + [OH^-]$

$$[NO_3^-] = 6.6 \times 10^{-7} M, [OH^-] = K_w/[H^+]$$

$$[H^+] = 6.6 \times 10^{-7} M + \frac{K_w}{[H^+]}$$

$$[H^+]^2 = 6.6 \times 10^{-7} M [H^+] + K_w$$

$$0 = [H^+]^2 - 6.6 \times 10^{-7} M [H^+] - K_w$$

Solve for $[H^+]$ using quadratic formula: $[H^+] = 6.7_5 \times 10^{-7}$ M, **pH = 6.17**

If total $[H^+] = 6.7_5 \times 10^{-7}$M, and HNO_3 contributes 6.6×10^{-7}M H^+, then the fraction of H^+ from nitric acid is:

$$\frac{6.6 \times 10^{-7}M}{6.7_5 \times 10^{-7}M} = \textbf{0.978 or 98\%}$$

5. What is the predominant species present in a solution of maleic acid that is buffered at pH 4.00? If the formal concentration of this solution is 0.125 M, what is the concentration of the predominant species at this pH? Maleic acid is **H**OOC(CH)$_2$COO**H**, but you can call this H_2A. K_{a1} = 1.20 x 10^{-2} and K_{a2} = 5.37 x 10^{-7}

pK_{a1} = -log(1.20x10^{-2}) = 1.92
pK_{a2} = -log(5.37x10^{-7}) = 6.27

At pH = pK_{a1} = 1.92, [H_2A] = [HA^-], while at pH = pK_{a2} = 6.27, [HA^-] = [A^{2-}]. Therefore, at an intermediate pH (such as 4.00), HA^- will be the predominant species. We can use an α calculation to figure out its concentration.

$$[HA^-] = (\alpha_{HA^-})F$$

$$\alpha_{HA^-} = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha_{HA^-} = \frac{10^{-4}(1.20x10^{-2})}{(10^{-4})^2 + 10^{-4}(1.20x10^{-2}) + (1.20x10^{-2})(5.37x10^{-7})} = 0.986$$

$$[HA^-] = (\alpha_{HA^-})F = 0.986 \times 0.125M = \mathbf{0.123\ M}$$

6. A weak diprotic acid, H_2A, has acid dissociation constants of $K_{a1} = 1.20 \times 10^{-2}$ and $K_{a2} = 5.37 \times 10^{-7}$. Calculate the pH and molar concentrations of H_2A, HA^-, and A^{2-} at equilibrium for a 0.125F solution of NaHA.

First find the $[H^+]$:

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = \sqrt{\frac{(1.20 \times 10^{-2})(5.37 \times 10^{-7})(0.125M) + (1.20 \times 10^{-2})(10^{-14})}{(1.20 \times 10^{-2}) + 0.125M}} = 7.67 \times 10^{-5}M$$

pH = -log(7.67x10⁻⁵) = 4.12 (you could also take the average of the pK_as and get nearly the same result (pH 4.09))

Once we have $[H^+]$, we can find the concentrations by determining the fraction of each species present. $[X] = \alpha_x F$.

$$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

In all cases, the denominator of the alpha expression is the same:

$d = [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}$
$= (7.67 \times 10^{-5})^2 + (1.20 \times 10^{-2})(7.67 \times 10^{-5}) + (1.20 \times 10^{-2})(5.37 \times 10^{-7}) = 9.327 \times 10^{-7}$

For H_2A:

$$\alpha_{H2A} = \frac{[H^+]^2}{d} = \frac{(7.67 \times 10^{-5})^2}{9.327 \times 10^{-7}} = 0.00631$$

and **$[H_2A] = \alpha_{H2A}F = 0.00631 \times 0.125M = 7.88 \times 10^{-4}$ M**

For HA^-:

$$\alpha_{HA-} = \frac{K_{a1}[H^+]}{d} = \frac{(1.20 \times 10^{-2})(7.67 \times 10^{-5})}{9.327 \times 10^{-7}} = 0.987$$

and **$[HA^-] = \alpha_{HA-}F = 0.987 \times 0.125M = 0.123$ M**

For A^{2-}:

$$\alpha_{A2-} = \frac{K_{a1}K_{a2}}{d} = \frac{(1.20 \times 10^{-2})(5.37 \times 10^{-7})}{9.327 \times 10^{-7}} = 0.00691$$

and **$[A^{2-}] = \alpha_{A2-}F = 0.00691 \times 0.125M = 8.64 \times 10^{-4}$ M**

Possibly Useful Information

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

Periodic Table of the Elements