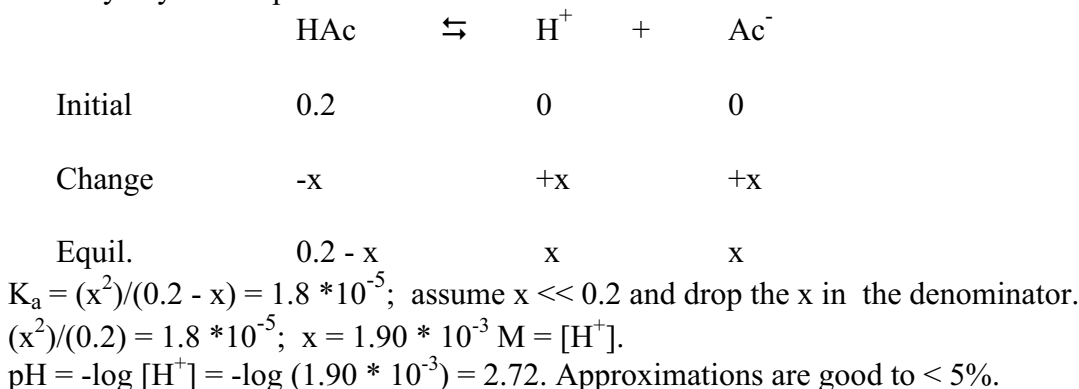


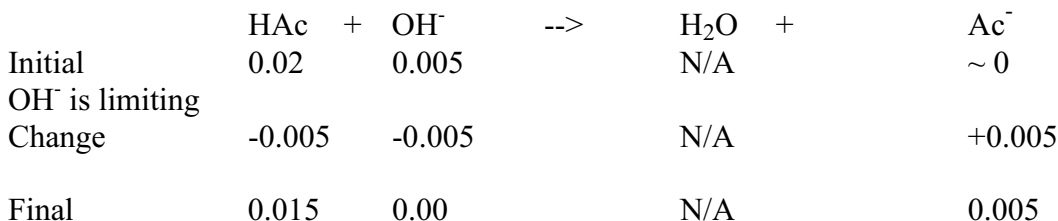
CHEM131 HOMEWORK #13 KEY

8-47.

a) You start with a solution containing 100 mL of 0.2 M Acetic acid, which I will abbreviate HAc. With no base added this is just a "simple" weak acid dissociation from the early days of chapter 7.



b) Now we have a stoichiometry problem first. If we add 50 mL of 0.100 M KOH, we are adding 0.050 L * 0.1 mol/L or 5 mmol KOH. We also know that since KOH is a strong base (i.e. strong electrolyte) in solution it completely dissociates such that we are adding 5 mmol of K⁺ and 5 mmol of OH⁻. The potassium is a spectator ion but the hydroxide is the strongest base and it will pull a proton from the best proton donor – i.e. the strongest acid, which is HAc. So, the stoichiometry problem is:



Remember these numbers are MOLES!

Our final concentrations are obtained by dividing by the volume of water

$$V = 50 \text{ mL} + 100 \text{ mL} = 150 \text{ mL} = 0.150 \text{ L.}$$

$$[\text{HAc}] = 0.1 \text{ M}, [\text{Ac}^-] = 0.033 \text{ M.}$$

We have an acid and a salt containing its conjugate base in high concentrations – this is a buffer!

We can use the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log ([\text{base}]/[\text{acid}]). \text{ Plugging in: } \text{pH} = 4.74 - 0.477 = 4.26.$$

c) The calculation proceeds the SAME as for part (b). Adding 100 mL of 0.1 M KOH means we added 10 mmol of OH⁻. This is 1/2 way to the equivalence point since we have neutralized 1/2 of the original acid. We have 10 mmol of acid left and 10 mmol of acetate ion created due to the neutralization by the strong base. Thus, $[\text{HAc}] = [\text{Ac}^-]$. $\text{pH} = \text{p}K_a = 4.74$

d) The calculation proceeds the SAME as for part (b). Adding 150 mL of 0.1 M KOH means we added 15 mmol of OH⁻. We have neutralized 15 mmol of the original acid. We have 5 mmol of acid left and 15 mmol of acetate ion created due to the neutralization by the strong base. [HAc] = 0.02 M, [Ac⁻] = 0.06 M (note – since the acid and base in a titration are in the same flask, they have the same volume which cancels out in the Henderson-Hasselbalch equation. This means you can take ratios of mols in solution and save time for (b) – (d)

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right). \text{ Plugging in: } \text{pH} = 4.74 + 0.477 = 5.22$$

e) This is the equivalence or stoichiometric point since the mol base added = mol acid in solution and all the acid is neutralized. Adding 200 mL of 0.1 M KOH means 20 mmol of OH⁻ were added, neutralizing the 20 mmol of HAc in solution. Again, proceeding as in part (b) we see that we have created 20 mmol of Ac⁻. To get the pH we have to realize that the major species are water and Ac⁻, but Ac⁻ is the conjugate base of a weak acid so it will react with the water. So, we have a hydrolysis problem! [Ac⁻]₀ = 0.02 mol/0.30 L = 0.067 M

	H ₂ O	+	Ac ⁻	⇌	OH ⁻	+	HAc
Initial			0.067		0		0
Change			-x		+x		+x
Equil.			0.067 - x		x		x

$K_b = (x^2)/(0.067 - x) = K_w/K_a = 1.0 * 10^{-14}/1.8 * 10^{-5}$; assume $x \ll 0.067$ and drop the x in the denominator.

$$(x^2)/(0.067) = 5.55 * 10^{-10}; \quad x = 6.1 * 10^{-6} \text{ M} = [\text{OH}^-].$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (6.1 * 10^{-6}) = 5.21$$

$$\text{pH} + \text{pOH} = 14.00, \text{ meaning } \text{pH} = 14.00 - 5.21 = 8.79.$$

Approximations are good to < 5%.

f) Now we have past the stoichiometric point and the pH is determined by the excess strong base that we have added. The stoichiometric calculations are the same as (b):

	HAc	+	OH ⁻	-->	H ₂ O	+	Ac ⁻
Initial	0.02		0.025		N/A		~ 0
HAc is limiting							
Change	-0.02		-0.02		N/A		+0.02
Final	0.00		0.005		N/A		0.02

Remember these numbers are MOLES!

Be a little careful here – our major species are Ac⁻ and OH⁻ and water. BUT OH⁻ is a STRONG base, while Ac⁻ is a (pretty) weak base. The pH in this case is ALWAYS determined by the strong base since the K_b for the strong base is $\gg 1$ and therefore is $\gg \gg$ K_b for the weak base – i.e. adding pure OH⁻ will determine the pH.

Our final concentrations are obtained by dividing by the volume of water

$$V = 250 \text{ mL} + 100 \text{ mL} = 350 \text{ mL} = 0.350 \text{ L.}$$

$$[\text{OH}^-] = 0.005/0.35 = 0.014 \text{ M}$$

$$\text{pOH} = 1.85 \text{ and the pH} = 12.15.$$

8-55. a) Let's backward plan this problem: We want the molar mass, but are given grams – so if we get the mol of our compound (mol NaA) we will have it solved. The compound is a strong electrolyte (salt) so we know that the mol of NaA = mol A^- in solution. Therefore we are looking for the mol A^- in solution. A^- is the anion of a weak acid, meaning it is a WEAK BASE.

The problem gives you that it took 1L of 0.1 M HCl to reach the stoichiometric point. This means that it took (1)(0.1) or 100 mmol of acid to neutralize the base. Thus, we know that we have 100 mmol of base, or mol $\text{A}^- = 0.100$. Thus, mol NaA = 0.1 and the molecular weight of NaA is 10.00g/0.1 mol or 100 g/mol.

b) To get the pH we need the K_b of the base or the K_a of the acid. However, this is not given so we have to figure it out. We are given that after adding 500 mL of 0.1 M HCl to 100 ml of the NaA solution the pH was 5.0. From (a) we know the mol of A^- in solution is 10.00 g/ 100 g/mol = 0.1 mol. From (b) we know that we added 0.5 L x 0.1 M = 0.05 mol HCl.

Remember – do the stoichiometric problem first (remember that HCl is a strong acid and completely dissociates into H^+ and Cl^-):

	H^+	+	A^-	-->	H_2O	+	HA
Initial	0.05		0.100		N/A		~ 0
H^+ is limiting							
Change	-0.05		-0.05		N/A		+0.05
Final	0.00		0.05		N/A		+0.05

(Remember these numbers are MOLES!)

Now for the equilibrium problem: Major species are A^- , HA and H_2O – we have a buffer!

We can use the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right). \text{ Since mol base} = \text{mol acid we find that } \text{pH} = \text{p}K_a = 5.0.$$

$$\text{Thus, } K_a = 10^{-5.0}.$$

Now we can solve the problem: at the stoichiometric point, all the A^- has been neutralized, i.e. converted to HA. So, we have 0.1 mol of HA in a volume of 1.00 + 0.100 L or V = 1.1 L. SO, $[\text{HA}]_0 = 0.091 \text{ M}$. Now solve the equilibrium problem:

	HA	\rightleftharpoons	H^+	+	A^-
Initial	0.091		~ 0		0
Change	-x		+x		+x

Equil. 0.091 - x x x

$K_a = (x^2)/(0.091 - x) = 1.0 * 10^{-5}$; assume $x \ll 0.091$ and drop the x in the denominator.

$(x^2)/(0.091) = 1.0 * 10^{-5}$; $x = 9.49 * 10^{-4} \text{ M} = [\text{H}^+]$.

$\text{pH} = -\log [\text{H}^+] = -\log (9.49 * 10^{-4}) = 3.02$. Approximations are good to $< 5\%$.

8-68. a) Now we have a polyprotic acid titration. We are given that $K_{a1} \gg K_{a2} \gg K_{a3}$ so that the pH of this solution is determined by the first dissociation only. In other words, the major species are water and H_3A .

	H_3A	\rightleftharpoons	H^+	+	H_2A^-
Initial	0.100		~ 0		0
Change	-x		+x		+x
Equil.	0.100 - x		x		x

$K_a = (x^2)/(0.100 - x) = 1.5 * 10^{-4}$; assume $x \ll 0.1$ and drop the x in the denominator.

$(x^2)/(0.100) = 1.5 * 10^{-4}$; $x = 3.87 * 10^{-3} \text{ M} = [\text{H}^+]$.

$\text{pH} = -\log [\text{H}^+] = -\log (3.87 * 10^{-3}) = 2.41$.

Approximations are : $3.87 * 10^{-3}/0.1 = 3.87\%$ so they are barely good to $< 5\%$.

b) Now we add 0.01 L x 1 M NaOH = 10 mmol of OH^- (NaOH is a strong base)
We have 0.100 L of 0.100 M acid which is 10 mmol of H_3A . Let's do the stoichiometry:

	OH^-	+	H_3A	\rightarrow	H_2O	+	H_2A^-
Initial	0.01		0.01		N/A		~ 0
Stoichiometric point!							
Change	-0.01		-0.01		N/A		+0.01
Final	0.00		0.00		N/A		+0.01

(Remember these numbers are MOLES!)

Now for the equilibrium problem: Major species are H_2A^- and H_2O – we have a buffer – but the acid and base is both H_2A^- ! This is the special case of the first stoichiometric point discussed in Zumdahl on page 315-316. In this case the pH is given by;

$\text{pH} = (\text{p}K_{a1} + \text{p}K_{a2})/2 = (3.82 + 7.52)/2 = 5.67$

c) Now we add 0.025 L x 1 M NaOH = 25 mmol of OH^- (NaOH is a strong base)

The first 10 mmol neutralize the acid H_3A producing 10 mmol H_2A^- as per (b), and 15 mmol OH^- are left over. The next 10 mmol of OH^- neutralize the 10 mmol of H_2A^- , producing 10 mmol HA^{2-} and leaving 5 mmol OH^- left over. Finally, we get to our last stoichiometric problem:

	OH^-	+	HA^{2-}	-->	H_2O	+	A^{3-}
Initial	0.005		0.01		N/A		~ 0
OH ⁻ is limiting							
Change	-0.005		-0.005		N/A		+0.005
Final	0.00		0.005		N/A		+0.005

(Remember these numbers are MOLES!)

The major species are water, HA^{2-} and A^{3-} . We have a "normal" buffer of a weak acid and a salt of its conjugate base. Now we can figure out the pH in the usual way:

$\text{pH} = \text{pK}_{\text{a}3} + \log([\text{base}]/[\text{acid}])$. Since mol base = mol acid we find that $\text{pH} = \text{pK}_{\text{a}3} = 11.3$.

Next H.W. Ch 8: 71, 73, 84, 91