CH116 Fall 2006 Prof. Sevian Solution to Group Problem 11/16/06

a) At this point, [HA] concentration is given and no OH⁻ has been added yet. So this is the **starting point** of the titration. Use the K_a reaction because this is a problem of HA dissociating slightly in water to make some H⁺, and we want to know pH.

	$\mathrm{HA}\left(aq\right) + \mathrm{H}_{2}\mathrm{O}\left(l\right) \leftrightarrows$	$A^{-}(aq)$	- $H_3O^+(aq)$
Initial	0.200 M	0	0
Change	- <i>x</i>	+x	+x
Equilibrium	$0.200 - x \approx 0.200$	x	x

Using the equilibrium constant expression:

$$K_a = \frac{\left[\mathrm{H}_3\mathrm{O}^+\right]\left[\mathrm{A}^-\right]}{\left[\mathrm{H}\mathrm{A}\right]} \approx \frac{(x)(x)}{(0.200)} = \frac{x^2}{0.200} = 1.9 \times 10^{-4} \quad \text{(which was given as the value for } K_a\text{)}$$

Solving for x, we get $x = \sqrt{(0.200)(1.9 \times 10^{-4})} = 6.16 \times 10^{-3} = [H_3O^+]$

Therefore, $pH = -\log [H_3O^+] = 2.21$

Note that the small x approximation is justified because x turned out to be on the order of 10^{-3} , so subtracting x from 0.200 would not make a significant change in the 0.200.

b) You can recognize this as the **titration midpoint** because 0.200 moles of HA were initially present and now 0.100 moles of OH⁻ have been added, so it's **halfway** to adding 0.200 moles of OH⁻ which would be the titration equivalence point.

At the titration midpoint, $pH = pK_a$ (note: if this were a base being titrated instead, and if you knew the K_b value, the fastest way to calculate pH would be from pOH = pK_b at titration midpoint)

$$pH = pK_a = -\log(1.9 \times 10^{-4}) = 3.72$$

c) You can recognize this as the **equivalence point** because exactly the same amount of OH⁻ has been added to equal the amount of HA that was initially present. [HA] = 0.200 M and [OH⁻] = 0.200 M. Since OH⁻ is strong, it reacts entirely, taking away the same amount of HA, to make A⁻. This describes the initial solution. Then A⁻ hydrolyzes slightly to make some OH⁻ at equilibrium.

Use the K_b reaction because you have HA, A⁻ and OH⁻ as the chemicals about which you know some information about concentrations. The solution described by the initial conditions above (with 0.200 M of A⁻ in it) is exactly as if you created a solution by adding 0.200 moles of A⁻ to 1 L of water.

	$A^{-}(aq) + H_2O(l)$	➡	HA (aq) +	$OH^{-}(aq)$
Initial	0 +0.200 M = 0.200 M		0.200 M - 0.200 M = 0	0.200 M - 0.200 M = 0
Change	- <i>x</i>		+ <i>x</i>	+ <i>x</i>
Equilibrium	$0.200 - x \approx 0.200$		X	X

This reaction has an equilibrium constant of K_b , which you can get from knowing K_a by using the equation that $K_aK_b = K_w$.

 $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.26 \times 10^{-11}$ (keep one more sig fig than needed for now, until we round later)

$$K_{a} = \frac{\left[\text{HA}\right]\left[\text{OH}^{-}\right]}{\left[\text{A}^{-}\right]} \approx \frac{(x)(x)}{(0.200)} = \frac{x^{2}}{0.200} = 5.26 \times 10^{-11}$$

Solving for *x*, we get $x = \sqrt{(0.200)(5.26 \times 10^{-11})} = 3.24 \times 10^{-6}$, which is the OH⁻ concentration

So, $pOH = -\log [OH^-] = 5.49$, and pH = 14 - pOH = 8.51. Note that this number has 2 sig figs (two digits after the decimal place) because the smallest number of sig figs in the given information was 2 sig figs in the value for K_a that was given.

Note that the small x approximation is justified because x turned out to be on the order of 10^{-6} , so subtracting x from 0.200 would not make a significant change in the 0.200.

d) You can recognize this as **after the equivalence point** because more OH^- has been added than the amount of HA initially present. The excess OH^- present is the amount beyond the equivalence point. Initially, there were 0.200 moles of HA present. So if 0.300 moles of OH^- have been added, there is an excess of 0.100 moles of OH^- . There is no need to set up the ICE table because *x* will be small, and adding *x* to the 0.100 moles of OH^- will not change the 0.100 moles of OH^- , so there is no need to calculate *x*.

$$[OH^{-}] = \frac{0.100 \text{ moles } OH^{-}}{1.00 \text{ L}} = 0.100 \text{ M}$$

 $pOH = -\log [OH^{-}] = 1.000$

pH = 14 - pOH = 13.000

e) The titration curve must be a graph of pH on the y-axis and amount of titrant (NaOH) added on the x-axis. Parts a, b, c and d above give four points (red diamonds) on this S-shaped curve, which are indicated in the graph below. The rest of the graph (blue line) is a sketch that connects these points to make an S-shaped curve which has an inflection point at the equivalence point of the titration.

