

### Problem Set 4 Solutions (For February 3)

1. The analytical concentration of the base is  $[B]_0 = 0.030$  M. From the equilibrium constant's magnitude (it's very small), we expect very little of the base to react. Consequently,  $[B]$  at equilibrium is very close to  $0.030$  M as well, and since there's no other source of  $BH^+$  or  $OH^-$ , these must have equal concentration at equilibrium (call this number  $x$ ). Thus, we can write  $K_b = [BH^+][OH^-]/[B] = x^2/0.030$ , and, solving for  $x$ ,  $x = [OH^-] = 2.79 \times 10^{-4}$  M. Since  $pH = 14.0 - pOH = 14.0 + \log([OH^-])$ , we find  $pH = 10.45$ . The numerator in the expression for  $\alpha$  is  $[BH^+] = [OH^-] = 2.79 \times 10^{-4}$  M. The denominator is the total base concentration in both forms,  $BH^+$  and  $B$ , which is  $0.030$  M. Thus,  $\alpha = (2.79 \times 10^{-4})/(0.030) = 9.31 \times 10^{-3}$ , or a bit less than 1%.

2. This problem is very much like the acetic acid/acetate buffer we discussed in class. We start by noting that  $0.5$  L of  $0.05$  M  $HC_2H_3O_2$  contain  $(0.5 \text{ L})(0.05 \text{ M}) = 25$  mmol  $HC_2H_3O_2$ . Similarly,  $5.74$  g  $NaC_2H_3O_2$  contain  $(5.74 \text{ g})/(82.03 \text{ g mol}^{-1}) = 70$  mmol  $C_2H_3O_2^-$ . Thus, the Henderson-Hasselbalch equation is

$$pH = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right) = 4.75 + \log\left(\frac{70 \text{ mmol}}{25 \text{ mmol}}\right) = 5.20$$

When we add  $50.0$  mL of  $0.01$  M  $NaOH$  to this buffer, we are adding  $(0.050 \text{ L})(0.01 \text{ M}) = 0.5$  mmol base as  $OH^-$ . This base will increase the amount of acetate ion by  $0.5$  mmol and lower the amount of acetic acid by  $0.5$  mmol, giving us  $70.5$  mmol acetate and  $24.5$  mmol acetic acid. Thus the final pH is

$$pH = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right) = 4.75 + \log\left(\frac{70.5 \text{ mmol}}{24.5 \text{ mmol}}\right) = 5.21$$

3. The pH of the solution,  $4.008$ , tells us  $[H^+]$  immediately:

$$[H^+] = 10^{-pH} = 10^{-4.008} = 9.817 \times 10^{-5} \text{ M}$$

This is significantly greater than the  $[H^+]$  contribution from water, so we are safe in assuming as well that the concentration of KHP's conjugate base anion (call it simply  $A^-$ ) must be the same: pure KHP dissolved in water is the only source for  $H^+$  and  $A^-$ . Likewise, the amount of molecular KHP (call it simply  $HA$ ) in the solution at equilibrium is the analytic concentration,  $[HA]_0 = 0.05000$  M, minus the  $A^-$  concentration,  $[A^-] = 9.817 \times 10^{-5}$  M, so that  $[HA] = [HA]_0 - [A^-]$ . Normally, because this is a weak acid, we say  $[A^-] \ll [HA]$  and  $[HA] = [HA]_0$ , but here we will include this small loss of  $HA$  because the precision of our input data requires it. We write

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(9.817 \times 10^{-5})^2}{0.05000 - 9.817 \times 10^{-5}} = 1.931 \times 10^{-7}$$

Had we made our usual approximation, we would find instead

$$K_a \cong \frac{[H^+][A^-]}{[HA]_0} = \frac{(9.817 \times 10^{-5})^2}{0.05000} = 1.927 \times 10^{-7}$$

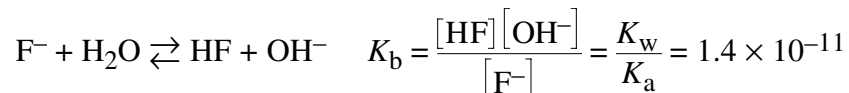
which isn't very much different, but the first result reflects the precision of our experimental data.

4. From the graph, we see that the equivalence point comes at  $20$  mL added base. This volume of base (with  $[OH^-] = 0.500$  M) contains  $(0.500 \text{ M})(0.020 \text{ L}) = 0.010$  mol  $OH^-$ . Thus, the initial solution must have contained  $0.010$  mol  $HF$  (that's what the equivalence point means, after all), and if the initial volume of  $HF$  solution was  $100.0$  mL, we find  $[HF]_0 = (0.010 \text{ mol})/(0.100 \text{ L}) = 0.10$  M. To calculate the initial pH, we look up the  $K_a$  value for  $HF$ , which is  $7.2 \times 10^{-4}$ , and calculate  $[H^+]$  in the usual way:

### Problem Set 4 Solutions (For February 3)

$$[\text{H}^+] = \sqrt{K_a [\text{HF}]_0} = \sqrt{(7.2 \times 10^{-4})(0.10)} = 8.5 \times 10^{-3} \text{ M}$$

or the  $\text{pH} = 2.08$ , as the graph suggests. After 10 mL of base have been added, we have diluted the solution a bit, *but we're at the 1/2 equivalence point*, and the  $\text{pH} = \text{p}K_a = 3.14$ ; dilution doesn't matter here (as long as the dilution isn't so huge that water self-ionization dominates  $[\text{H}^+]$ , which we are safe in ignoring here). At the equivalence point, we have a solution of total volume 100.0 mL + 20 mL = 120 mL which now contains the conjugate base  $\text{F}^-$  as the dominant species in an amount very closely given by the amount of HF at the start of the titration: 0.010 mol. Here, we have created a solution of NaF ( $\text{Na}^+ + \text{F}^-$ ) in which  $[\text{F}^-]_0 = (0.010 \text{ mol})/(0.120 \text{ L}) = 0.083 \text{ M}$ . This weak base,  $\text{F}^-$ , is hydrolyzed according to the base hydrolysis expression we derived in class:



We assume  $[\text{HF}] = [\text{OH}^-]$  and  $[\text{F}^-] = [\text{F}^-]_0$  and find first the hydroxide concentration:

$$[\text{OH}^-] = \sqrt{K_b [\text{F}^-]_0} = \sqrt{(1.4 \times 10^{-11})(0.083)} = 1.1 \times 10^{-6} \text{ M}$$

which tells us  $\text{pOH} = -\log[\text{OH}^-] = 5.96$  so that  $\text{pH} = 14.0 - \text{pOH} = 8.04$ , decidedly basic, as we expected for the equivalence point of a weak acid titrated by a strong base. After 30 mL of base has been added, we are well past the equivalence point, the volume is 130 mL, and the solution is dominated by the excess base added *beyond* the equivalence point. This excess (10 mL worth) contains  $(0.500 \text{ M})(0.010 \text{ L}) = 5 \text{ mmol OH}^-$ , and at this last point in the titration, we can say that  $[\text{OH}^-] = (0.005 \text{ mol})/(0.130 \text{ L}) = 0.038 \text{ M}$  for a  $\text{pOH} = 1.4$  and a  $\text{pH}$  of 12.6, again in agreement with the graph!

5. (a) Each mole of salicylic acid produces one mole of aspirin. Thus the maximum yield of aspirin is

$$m = nM = (0.045 \text{ mol})(180.16 \text{ g mol}^{-1}) = 8.11 \text{ g}$$

(b) First, we calculate  $[\text{H}^+]$  from the  $\text{pH}$ ;

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.19} = 6.46 \times 10^{-4} \text{ M}$$

Calling aspirin HA and its conjugate base  $\text{A}^-$ , we know  $[\text{H}^+] = [\text{A}^-]$ , and we also know that the analytic concentration of aspirin,  $[\text{HA}]_0$ , is related to the equilibrium concentration  $[\text{HA}]$  through  $[\text{HA}] = [\text{HA}]_0 - [\text{A}^-]$ . We seek  $[\text{HA}]_0$ , which we find from

$$K_a = 2.75 \times 10^{-5} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.46 \times 10^{-4})^2}{[\text{HA}]_0 - 6.46 \times 10^{-4}} \quad \text{so that} \quad [\text{HA}]_0 = 0.0158 \text{ M}$$

(If we neglect the  $6.46 \times 10^{-4}$  in the denominator, we find  $[\text{HA}]_0 = 0.0151 \text{ M}$ .) Thus, the amount of aspirin dissolved in 1.00 L must have been 0.0158 mol, which weighs  $(0.0158 \text{ mol})(180.16 \text{ g mol}^{-1}) = 2.85 \text{ g}$ . The yield is

$$\frac{2.85 \text{ g}}{8.11 \text{ g}} \times 100\% = 35.1\%$$