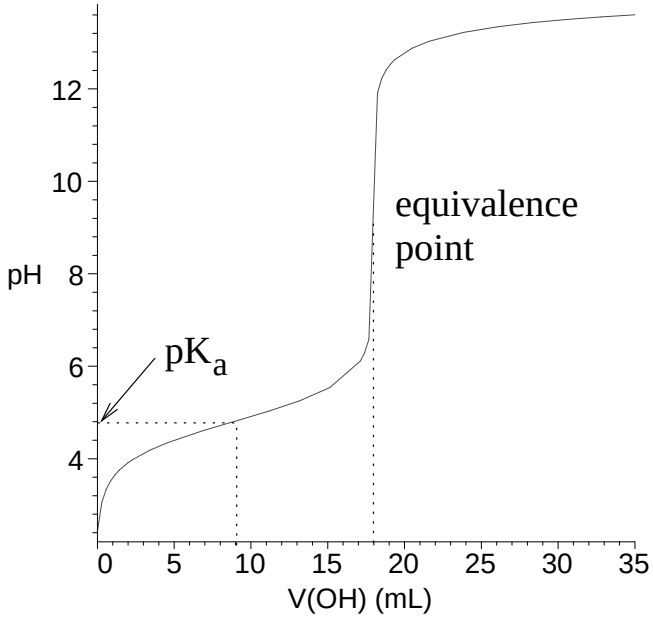
Chemistry 2000B Spring 2002 Assignment 3 Solutions

1. We first have to find the equivalence point:



When half the acid has been neutralized, the *p*H equals the pK_a. Since the equivalence point is at 18 mL, the pK_a is the *p*H at 9 mL of hydroxide solution added. From the graph, we find

$$\begin{aligned} pK_a &\approx 4.8. \\ \therefore K_a &= 10^{-4.8} = 1.58 \times 10^{-5}. \end{aligned}$$

2. The weak base nitrite will react with the strong acid stoichiometrically:

$$NO_2^- + H^+ \rightarrow HNO_2.$$

We must determine which reagent is in excess.

$$\begin{aligned} n_{NO_2^-} &= \frac{m_{NaNO_2}}{M_{NaNO_2}} = \frac{3.75\,\text{g}}{68.9953\,\text{g/mol}} = 0.0544\,\text{mol}. \\ n_{H^+} &= (0.85\,\text{mol/L})(0.065\,\text{L}) = 0.0553\,\text{mol}. \end{aligned}$$

The hydrogen ions are in excess by 8.98×10^{-4} mol. Normally in these problems, the excess protons determine the *p*H. In other words, we ignore the dissociation of the acid. If we can do this, the concentration of H^+ in solution is just

$$[H^+] = \frac{8.98 \times 10^{-4}\,\text{mol}}{0.065\,\text{L}} = 1.38 \times 10^{-2}\,\text{mol/L}.$$

Is it legitimate to ignore the dissociation of the acid? The K_a expression for nitrous acid is

$$K_a = \frac{(a_{NO_2^-})(a_{H^+})}{a_{HNO_2}}$$

or

$$\frac{a_{NO_2^-}}{a_{HNO_2}} = \frac{K_a}{a_{H^+}}.$$

Assuming that a_{H^+} is approximately 1.38×10^{-2} (as calculated above), we have

$$\frac{a_{NO_2^-}}{a_{HNO_2}} = \frac{4.5 \times 10^{-4}}{1.38 \times 10^{-2}} = 0.033.$$

In other words, about 3% of the nitrous acid formed will dissociate. The concentration of nitrous acid, again neglecting dissociation, is $0.0544\,\text{mol}/0.065\,\text{L} = 0.84\,\text{mol}/\text{L}$ so dissociation of the acid would product about $0.027\,\text{mol}/\text{L}$ of additional protons. This is *bigger* than the number of excess protons, so we can't really neglect this. There are two ways to deal with this problem, both of which revolve around the K_a expression:

(a) Go back to the beginning. The initial concentrations of H^+ and of nitrite are, respectively, 0.85 mol/L and $0.0544\,\text{mol}/0.065\,\text{L} = 0.836\,\text{mol}/\text{L}$.

	a_{H^+}	$a_{NO_2^-}$	a_{HNO_2}
Initial	0.85	0.836	0
Change	$-x$	$-x$	x
Final	$0.85-x$	$0.836-x$	x

Therefore,

$$\begin{aligned} K_a &= 4.5 \times 10^{-4} = \frac{(a_{NO_2^-})(a_{H^+})}{a_{HNO_2}} = \frac{(0.836-x)(0.85-x)}{x}. \\ \therefore 4.5 \times 10^{-4} x &= 0.711 - 1.686x + x^2. \\ \therefore 0 &= x^2 - 1.687x + 0.711. \\ \therefore x &= 0.864 \text{ or } 0.823. \end{aligned}$$

The second solution has to be the right one, otherwise the concentrations of H^+ and of NO_2^- turn out negative. We therefore have

$$\begin{aligned} a_{H^+} &= 0.85 - 0.823 = 0.0273. \\ \therefore p\text{H} &= 1.56. \end{aligned}$$

(b) The other approach is to assume that the reaction goes to completion, and then to calculate how much dissociation occurs "after" that. Of course, it doesn't actually

happen that way, but it works just as well from the point of view of calculating the concentrations at equilibrium. In this case, we would take $[H^+] = 1.38 \times 10^{-2}\,\text{mol/L}$ and $[HNO_2] = 0.836\,\text{mol/L}$ (the concentration generated by the reaction if it goes to completion). Then our table is

	a_{H^+}	$a_{NO_2^-}$	a_{HNO_2}
Initial	1.38×10^{-2}	0	0.836
Change	x	x	$-x$
Final	$1.38 \times 10^{-2} + x$	x	$0.836 - x$

$$\begin{aligned} \therefore K_a &= 4.5 \times 10^{-4} = \frac{(a_{NO_2^-})(a_{H^+})}{a_{HNO_2}} = \frac{x(1.38 \times 10^{-2} + x)}{0.836 - x}. \\ \therefore 4.5 \times 10^{-4}(0.836 - x) &= x(1.38 \times 10^{-2} + x). \\ \therefore 0 &= x^2 + 1.43 \times 10^{-2}x - 3.76 \times 10^{-4}. \\ \therefore x &= -2.78 \times 10^{-2} \text{ or } 1.35 \times 10^{-2}. \end{aligned}$$

Again, the second solution is the correct one. It follows that $a_{H^+} = 1.38 \times 10^{-2} + 1.35 \times 10^{-2} = 2.74 \times 10^{-2}$, so that the pH is 1.56.

3. The sodium nitrate is irrelevant[1] since nitrate is the conjugate base of a strong acid. Accordingly,

$$p\text{H} = -\log_{10} a_{H^+} = -\log_{10}(0.85) = 0.07.$$

4. The titration used

$$n_{OH^-} = (1.43\,\text{mol/L})(94.40 \times 10^{-3}\,\text{L}) = 0.135\,\text{mol}.$$

At the equivalence, point, $n_{OH^-} = n_{\text{acid}}$. The molar mass of the acid is therefore

$$M = \frac{10.05\,\text{g}}{0.135\,\text{mol}} = 74.4\,\text{g/mol}.$$

5. (a) The K_a of the ammonium ion is 5.6×10^{-10}. Since we want the pH to be 9, the activity of the hydrogen ion will be $a_{H^+} = 10^{-9}$. We can calculate the desired ratio of ammonia and ammonium:

$$\begin{aligned} K_a &= \frac{(a_{NH_3})(a_{H^+})}{a_{NH_4^+}}. \\ \therefore \frac{a_{NH_3}}{a_{NH_4^+}} &= \frac{K_a}{a_{H^+}} = \frac{5.6 \times 10^{-10}}{10^{-9}} = 0.56. \end{aligned}$$

[1] There can be a small effect since solutes in general change the volume of the solution, but this is an *extremely* small effect.

Suppose that we take 1 L of the ammonia solution. This would contain 0.0435 mol of ammonia. Since the ratio of the activities is the same as the ratio of the number of moles, we want

$$n_{NH_4^+} = \frac{n_{NH_3}}{0.56} = \frac{0.0435\,\text{mol}}{0.56} = 0.0777\,\text{mol}.$$

From the number of moles of ammonium, we can calculate the mass of ammonium chloride required:

$$m_{NH_4Cl} = (0.0777\,\text{mol})(53.4910\,\text{g/mol}) = 4.16\,\text{g}.$$

The procedure for making our buffer is therefore as follows:

i. Measure 1 L of the ammonia solution.
ii. Dissolve 4.16 g of ammonium chloride into the ammonia solution.
iii. Adjust the *p*H with HCl or ammonia solution, as appropriate.

(b) The buffer solution contains 0.0435 mol/L ammonia and 0.0777 mol/L ammonium ion. 50 mL of this solution therefore contains

$$\begin{aligned} n_{NH_3} &= (0.0435\,\text{mol/L})(0.050\,\text{L}) = 2.175\times10^{-3}\,\text{mol}. \\ n_{NH_4^+} &= (0.0777\,\text{mol/L})(0.050\,\text{L}) = 3.884\times10^{-3}\,\text{mol}. \end{aligned}$$

5 mL of 0.20 mol/L sodium hydroxide solution contains

$$n_{OH^-} = (0.005\,\text{L})(0.20\,\text{mol/L}) = 1.0\times10^{-3}\,\text{mol}.$$

The hydroxide will react with the ammonium:

$$NH_4^- + OH^- \rightarrow NH_3 + H_2O.$$

The final numbers of ammonium and of hydroxide ions after reaction are therefore

$$\begin{aligned} n_{NH_3} &= 2.175\times10^{-3} + 1.0\times10^{-3}\,\text{mol} = 3.175\times10^{-3}\,\text{mol}. \\ n_{NH_4^+} &= 3.884\times10^{-3}\,\text{mol} - 1.0\times10^{-3}\,\text{mol} = 2.884\times10^{-3}\,\text{mol}. \\ \text{But since } K_a &= \frac{(a_{NH_3})(a_{H^+})}{a_{NH_4^+}}, \\ a_{H^+} &= K_a\frac{a_{NH_4^+}}{a_{NH_3}} \\ &= (5.6\times10^{-10})\frac{2.884\times10^{-3}\,\text{mol}}{3.175\times10^{-3}\,\text{mol}} = 5.09\times10^{-10}. \\ \therefore\, p\text{H} &= -\log_{10} a_{H^+} = 9.29. \end{aligned}$$

6. $H_2PO_4^-$ and HCO_3^- are both amphoteric species. The question we must first ask ourselves is which one is the strongest base and which the strongest acid? We look up these two species in the table of ionization constants (table 17.4) in the textbook. We find the following:

	$H_2PO_4^-$	HCO_3^-
K_a	6.2×10^{-8}	4.8×10^{-11}
K_b	1.3×10^{-12}	2.4×10^{-8}

$H_2PO_4^-$ is the strongest acid (largest K_a) and HCO_3^- is the strongest base (largest K_b). Thus, in the first, instance, we might see these two species react together. To analyze this reaction, we consider the relevant ionization reactions:

$$\begin{array}{rcll} H_2PO_4^- & \rightarrow & HPO_4^{2-} + H^+ & K_1 = 6.2\times10^{-8} \\ HCO_3^- + H_2O & \rightarrow & H_2CO_3 + OH^- & K_2 = 2.4\times10^{-8} \\ H^+ + OH^- & \rightarrow & H_2O & K_3 = 1/K_w = 10^{14} \\ \hline H_2PO_4^- + HCO_3^- & \rightarrow & HPO_4^{2-} + H_2CO_3 & K = K_1K_2K_3 = 0.149. \end{array}$$

We now have the overall reaction and its equilibrium constant. The rest is a standard equilibrium problem, give or take that we need to take the dilution on mixing the two solutions into account. Initially, we have

$$\begin{aligned} [H_2PO_4^-] &= \frac{c_1V_1}{c_2} = \frac{(0.043\,\text{mol/L})(15\,\text{mL})}{15+25\,\text{mL}} = 0.0161\,\text{mol/L}. \\ [HCO_3^-] &= \frac{(0.54\,\text{mol/L})(25\,\text{mL})}{40\,\text{mL}} = 0.338\,\text{mol/L}. \end{aligned}$$

We can now construct the following table:

	$H_2PO_4^-$	HCO_3^-	HPO_4^{2-}	H_2CO_3
Initial	0.0161	0.338	0	0
Change	$-x$	$-x$	x	x
Final	$0.0161-x$	$0.338-x$	x	x

The equilibrium condition is therefore

$$\begin{aligned} K &= 0.149 = \frac{(a_{HPO_4^{2-}})(a_{H_2CO_3})}{(a_{H_2PO_4^-})(a_{HCO_3^-})} = \frac{x^2}{(0.0161-x)(0.338-x)}. \\ \therefore x^2 &= 0.149(0.0161-x)(0.338-x) \\ &= 0.149(5.44\times10^{-3} - 0.354x + x^2) \\ &= 8.10\times10^{-4} - 0.0526x + 0.149x^2. \\ \therefore 0 &= 0.851x^2 + 0.0526x - 8.10\times10^{-4}. \\ \therefore x &= \frac{-0.0526 + \sqrt{(0.0526)^2 - 4(0.851)(-8.10\times10^{-4})}}{2(0.851)} = 0.0128. \\ \therefore [HPO_4^{2-}] &= [H_2CO_3] = 0.0128\,\text{mol/L}, \\ [H_2PO_4^-] &= 0.0161 - 0.0128\,\text{mol/L} = 0.0034\,\text{mol/L}, \\ \text{and } [HCO_3^-] &= 0.338 - 0.0128\,\text{mol/L} = 0.325\,\text{mol/L}. \end{aligned}$$