Additional Problems: Answers

1. A buffered solution is made by adding 75.0 grams of sodium acetate to 500 mL of a 0.64M solution of acetic acid at 25°C. What is the pH of the final solution? (assume no volume change). $K_a (\text{CH}_3\text{CO}_2\text{H}) = 1.8 \times 10^{-5}$

75 g (CH$_3$CO$_2$Na) F.W. = 82 g/mol = 0.914 mol/0.5L = 1.8 M

CH$_3$CO$_2$H (aq) + H$_2$O(l) $\rightleftharpoons$ CH$_3$CO$_2$- (aq) + H$_3$O$^+$ (aq)

Initial: 0.64M 1.8M $10^{-7}$M

$K_a = 1.8 \times 10^{-5} = [\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+] / [\text{CH}_3\text{CO}_2\text{H}]$

Henderson-Hasselbach equation: $pH=pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$

Concentrations of $[\text{A}^-]_o, [\text{HA}]_o$ are within an order of magnitude

$[\text{A}^-]_o = [\text{CH}_3\text{CO}_2^-] = 1.8 \text{M}$ ; $[\text{HA}]_o = [\text{CH}_3\text{CO}_2\text{H}] = 0.64 \text{M}$

$pH= 4.74 + \log [1.8 \text{M}/0.64 \text{M}] = 5.2$

2. Calculate the pH after 0.01 mol of gaseous HCl is added to 250mL of each of the following solutions: $K_b (\text{NH}_3) = 1.8 \times 10^{-5}$

a.) 0.05M NH$_3$ and 0.15M NH$_4$Cl

NH$_3$ (aq) + H$_2$O(l) $\rightleftharpoons$ NH$_4^+$ (aq) + HO(aq)

Initial: 0.0125 mol 0.0375 mol

Final: 0.0025 mol 0.0475 mol

Final: 0.01 M 0.19 M

Concentrations are slightly greater than an order of magnitude different so we can try H-H equation:

$pOH = pK_b + \log [\text{HB}/B] = 4.74 + \log [0.19 \text{M}/0.01 \text{M}] = 6.02$; $pH=14-6.02= 7.9$

since $[\text{OH}]$~ $10^{-7}$ and $[\text{H}_3\text{O}^+]$~ $10^{-8}$ << 0.01M and 0.19M, H-H is ok.

b.) 0.50 M NH$_3$ and 1.50M NH$_4$Cl

NH$_3$ (aq) + H$_2$O(l) $\rightleftharpoons$ NH$_4^+$ (aq) + HO(aq)

Initial: 0.125 mol 0.375 mol

Final: 0.115 mol 0.385 mol

Final: 0.46 M 1.54 M

$pOH = pK_b + \log [\text{HB}/B] = 4.74 + \log [1.54 \text{M}/0.46 \text{M}]=5.26$; $pH= 8.7$

since $[\text{OH}]$= $10^{6}$ and $[\text{H}_3\text{O}^+]$~$10^{-9}$<< 0.46M and 1.54M, H-H is ok.

3. A student has prepared 1L of a buffer solution containing 0.10M HCN and 0.12 M CN$^-$. $K_a = 7.2 \times 10^{-10}$

(a) what is the pH of this buffer?

H-H should be fine: $pH=pK_a + \log [\text{CN}]/[\text{HCN}] = 9.14 + \log [0.12 \text{M}/0.1 \text{M}] = 9.2$

(b) What is the pH if 0.01 mol of HCl is added to the buffer?

HCN(aq) + H$_2$O (l) $\rightleftharpoons$ CN$^-$ (aq) + H$_3$O$^+$ (aq)

Initial: 0.1M 0.12M $10^{-7}$M

Final: 0.11M 0.11M

$PH= pK_a + \log [\text{CN}]/[\text{HCN}] = 9.14 + \log [0.11 \text{M}/0.11 \text{M}] = 9.14$
(c) What is the pH if 0.02 mol of NaOH is added to the original buffer?

\[ \text{HCN}(aq) + H_2O (l) \rightleftharpoons \text{CN}^- (aq) + H_3O^+ (aq) \]

Initial: \[ 0.1 \text{M} \quad 0.12 \text{M} \quad 10^{-7} \text{M} \]
Final: \[ 0.08 \text{M} \quad 0.14 \text{M} \]

\[ \text{pH} = \text{pK}_a + \log \left[ \frac{[\text{CN}^-]}{[\text{HCN}]} \right] = 9.14 + \log \left[ \frac{0.14 \text{M}}{0.08 \text{M}} \right] = 9.38 \]

4. A 310 mg sample of a weak, monoprotic acid was dissolved in sufficient water to prepare 100 mL of solution. It was found that 25.15 mL of a standard 0.1 M sodium hydroxide solution neutralized the acid to the equivalence point. What is the apparent molecular weight of the unknown acid?

\[ (25.15 \text{ mL})(1 \text{L}/1000 \text{mL}) (0.1 \text{ M NaOH}) = 0.002515 \text{ mol NaOH required to neutralize acid.} \]
\[ (310 \text{ mg})(1 \text{ g}/1000 \text{mg}) = 0.310 \text{ g} / 0.002515 \text{ mol} = 123.3 \text{ g/mol} \]

5. A solution of a certain weakly acidic substance was prepared by dissolving and diluting 2.344 g to a final volume of 100 mL. In a titration, 42.6 mL of 0.2500 M NaOH solution was required to reach a successful endpoint. The shape of the titration curve was used for the assumption that the acid was monoprotic. The pH at the endpoint was 9.4.

(a) Calculate the apparent molecular weight of the unknown acid.

\[ (0.0426 \text{ L})(0.25 \text{ M NaOH}) = 0.01065 \text{ mol required to reach endpoint.} \]
\[ 2.344 \text{ g} / 0.01065 \text{ mol} = 220 \text{ g/mol} \]

(b) Calculate the \( K_a \) for the acidic substance

At endpoint: \[ [A^-] = 0.01065/0.1426 \text{ L} = 0.075 \text{ M}; \text{pOH}=14-9.4 =4.6 \]

At endpoint: \[ A^-(aq) + H_2O (l) \rightleftharpoons HA (aq) + HO^-(aq) \]

Initial: \[ 0.075 \text{M} \quad 0 \text{M} \quad 10^{-7} \text{M} \]
Eqil: \[ 0.0749 \text{M} \quad 2.5 \times 10^{-5} \text{M} \quad 2.5 \times 10^{-5} \text{M} \]

\[ K_b = [HA]_{eq}[OH]_{eq}/[A^-]_{eq} = (2.5 \times 10^{-5} \text{M})^2/0.0749 \text{M} = 8.34 \times 10^{-9}; \text{K}_a = 1.2 \times 10^{-6} \]

(c) Calculate the pH of the original 100 mL solution (prior to titration)

\[ \text{HA} + H_2O (l) \rightleftharpoons H_3O^+ (aq) + A^-(aq) \]

Initial: \[ 0.1065 \text{M} \quad 10^{-7} \text{M} \quad 0 \text{M} \]
Eq.: \[ 0.1065 -x \quad 10^{-7} + x \quad x \]

\[ K_a = [A^-]_{eq}[H_3O^+]_{eq}/[HA]_{eq} = 1.2 \times 10^{-6} = (10^{-7}+x)(x)/0.1065 -x \]

\[ 1.278 \times 10^{-7} - 1.2 \times 10^{-6}x = 10^{-7}x + x^2; x^2+1.3 \times 10^{-6}x - 1.278 \times 10^{-7} = 0 \]

quadratic: \[ x=3.56 \times 10^{-4}; [H_3O^+] = 3.57 \times 10^{-4}; \text{pH}= 3.44 \]

(d) Calculate the pH at the midpoint of the titration (after addition of 21.3 mL of the sodium hydroxide solution)

At midpoint of titration, \[ [A^-] = [HA] \] and \text{pH}=\text{pKa}

Since \( K_a = 1.2 \times 10^{-6} \), \text{pKa}= 5.92

(e) Carefully construct a graph of pH vs. mL of base added for the titration. What would be a suitable indicator for the titration? Use text Figure 17.6 for reference. Note that the initial pH, volume added to reach equivalence point, and equivalence point pH are
different than that represented in Fig 17.6. phenolphthalein is probably the best indicator.

6. Calculate the ratio of $[\text{NH}_3]/[\text{NH}_4^+]$ in each of the following buffered solutions containing ammonia and ammonium chloride.
   
   a. pH=9.00
   
   since these are all buffers, we can use H-H:
   $$\text{pH}= \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad \text{pK}_a = -\log 5.6 \times 10^{-10} = 9.25$$
   $$\text{pH}= 9 = 9.25 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad [\text{NH}_3]/[\text{NH}_4^+]= 0.56$$
   
   b. pH=8.80
   $$\text{pH}= 8.8 = 9.25 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad [\text{NH}_3]/[\text{NH}_4^+]= 0.35$$
   
   c. pH=10.5
   $$\text{pH}= 10.5 = 9.25 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad [\text{NH}_3]/[\text{NH}_4^+]= 17.7$$

7. A sample of 25 mL of 0.100M NH$_3$ ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.100M HCl. Calculate the pH of the sample if you added a TOTAL volume of:
   
   a. 0.00mL of the 0.10 M HCl to your sample
   
   Initial: $0.1\text{M}$ $0\text{M}$ $10^{-7}\text{M}$
   
   Final: $0.1-x$ $x$ $10^{-7} + x$
   
   $K_b = [\text{NH}_4^+]_{eq}/[\text{NH}_3]_{eq} = (x)(10^{-7} + x)/(0.1-x) = 1.8 \times 10^{-5}$
   
   Assume $x<<0.1; \quad 10^{-7}x + x^2 = 1.8 \times 10^{-6}; \quad x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-6} = 0$
   
   Quadratic: $x=0.00134$ (1.3% of 0.1M; 1% is usually the cutoff)
   
   Solve exactly: $10^{-7}x + x^2 = 1.8 \times 10^{-6} - 1.8 \times 10^{-5}x$; $x^2 + 1.81 \times 10^{-5}x - 1.8 \times 10^{-6} = 0$
   
   $x = 0.00133$ $[\text{HO}^-] = 0.00133$ M $; [\text{H}_3\text{O}^+] = 7.52 \times 10^{-12}$ M; pH=11.12

   b. 8.0 mL of the 0.1M HCl to your sample (0.008L*0.1M = 8x10^{-4}mol HCl added. Note: all HCl added reacts with NH$_3$ to produce NH$_4^+$; this is a stoichimetry problem initially. Remember volumes when calculating concentrations!)

   Initial: $0.0025\text{mol}$ $0\text{M}$ $10^{-7}\text{M}$
   
   Final: $0.0017\text{ mol}$ $0.0008\text{ mol}$
   
   Final: $0.052\text{ M}$ $0.024\text{M}$
   
   $p\text{OH} = \text{pK}_b + \log [\text{NH}_4^+]/[\text{NH}_3] = 4.74 + \log (0.024\text{M})/(0.052\text{M}) = 4.4$
   
   pH=14-p\text{OH} = 9.6

   c. 12.5 mL of the 0.10 M HCl to your sample

   Initial: $0.0025\text{mol}$ $0\text{M}$ $10^{-7}\text{M}$
   
   Final: $0.0012\text{ mol}$ $0.00128\text{ mol}$
   
   Final: $0.0325\text{ M}$ $0.0341\text{M}$
   
   $p\text{OH} = \text{pK}_b + \log [\text{NH}_4^+]/[\text{NH}_3] = 4.74 + \log (0.034\text{M})/(0.033\text{M}) = 4.76$
   
   pH=14-p\text{OH} = 9.24
d. 25 mL of the 0.10 M HCl to your sample.

\[ \text{NH}_3 \text{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ \text{(aq)} + \text{HO}^- \text{(aq)} \]

Initial: 0.0025 mol, 0 M, $10^{-7}$ M
Final: 0 mol, 0.025 mol

\[ \text{NH}_4^+ \text{(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3 \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)} \]

Initial: 0.05 M, 0 M, $10^{-7}$ M
Final: 0.05 - x, x, $10^{-7} + x$

\[ K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3]_{eq}[\text{H}_3\text{O}^+]_{eq}}{[\text{NH}_4^+]_{eq}} = \frac{(x)(10^{-7} + x)}{(0.05 - x)} \]

Assume x << 0.05; \( x^2 + 10^{-7}x = 2.8 \times 10^{-11} \); \( x^2 + 10^{-7}x - 2.8 \times 10^{-11} = 0 \)

Quadratic: \( x = 5.25 \times 10^{-6} \)

\[ [\text{H}_3\text{O}^+] = 10^{-7} + x = 5.34 \times 10^{-6} \]; pH = **5.27**