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 (CH_3CO_2H) = $1.8x10^{-5}$
   75 g (CH_3CO_2Na) F.W. =82 g/mol =0.914 mol/0.5L = 1.8 M

   CH_3CO_2H (aq) + H_2O(l) ⇔ $CH_3CO_2^-$ (aq) + H_3O^+(aq)
   Initial: 0.64M 1.8M 10^{-7}M
   $K_a = 1.8 \times 10^{-5} = [CH_3CO_2^-][H_3O^+] / [CH_3CO_2H] =$
   Henderson-Hasselbach equation: pH=pKa + log $[A^-]_o/[HA]_o$
   Concentrations of $[A^-]_o$,$[HA]_o$ are within an order of magnitude
   $[A^-]_o = [CH_3CO_2^-] = 1.8M$; $/[HA]_o = [CH_3CO_2H] = 0.64M$
   pH= 4.74 + log [1.8M/0.64M] = 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 (NH_3) =$1.8x10^{-5}$
   a.) 0.05M NH_3 and 0.15M NH_4Cl
   NH_3 (aq) + H_2O(l) ⇔ NH_4^+ (aq) + HO^-(aq)
   Initial: 0.0125mol 0.0375mol
   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 [HB/B] = 4.74 + log [0.19M/0.01M] = 6.02; pH=14-6.02= 7.9
   since [HO]~ 10^{-7} and $[H_3O^+]$~10^{-8} << 0.01M and 0.19M, H-H is ok.

   b.) 0.50 M NH_3 and 1.50M NH_4Cl
   NH_3 (aq) + H_2O(l) ⇔ NH_4^+ (aq) + HO^-(aq)
   Initial: 0.125mol 0.375 mol
   Final: 0.115 mol 0.385 mol
   Final: 0.46 M 1.54M
   pOH = pK_b + log [HB/B] = 4.74 + log [1.54M/0.46M]=5.26; pH= 8.7
   since [OH]=10^6 and $[H_3O^+]$~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 x 10^{-10}
   (a) what is the pH of this buffer?
   H-H should be fine: pH=pK_a + log [CN]/[HCN] = 9.14 + log [.12M/.1M] = 9.2
   (b) What is the pH if 0.01 mol of HCl is added to the buffer?
   HCN(aq) + H_2O (l) ⇔ CN^- (aq) + H_3O^+(aq)
   Initial: 0.1M 0.12M 10^{-7}M
   Final: 0.11M 0.11M
   PH= pK_a + log [CN]/[HCN] = 9.14 + log [0.11M/0.11M] = 9.14

(c) What is the pH if 0.02 mol of NaOH is added to the original buffer?

$HCN(aq) + H_2O(l) \Leftrightarrow CN^-(aq) + H_3O^+(aq)$

Initial:	0.1M	0.12M	10^{-7}M
Final:	0.08M	0.14M	

$pH = pK_a + \log [CN]/[HCN] = 9.14 + \log [0.14M/0.08M] = 9.38$

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 25.15mL of a standard 0.1M sodium hydroxide solution neutralized the acid to the equivalence point. What is the apparent molecular weight of the unknown acid?

   (25.15 mL)(1L/1000mL) (0.1M NaOH) = 0.002515 mol NaOH required to neutralize acid. (310mg)(1g/1000mg)= 0.310g / 0.002515mol = **123.3 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 100mL. In a titration, 42.6 mL of 0.2500M 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.

   (0.0426L)(0.25M NaOH) = 0.01065 mol required to reach endpoint. 2.344g/0.01065 mol =**220 g/mol**

   (b) Calculate the K_a for the acidic substance

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

   At endpoint: $A^-(aq) + H_2O(l) \Leftrightarrow HA(aq) + HO^-(aq)$

Initial:	0.075M	0M	10^{-7}M
Equil:	0.0749M	2.5×10^{-5}M	2.5×10^{-5}M

$K_b = [HA]_{eq}[^-OH]_{eq}/[A^-]_{eq} = (2.5\times10^{-5}M)^2/0.0749M = 8.34\times10^{-9}$; $K_a = 1.2 \times10^{-6}$

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

   $HA + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq)$

Initial:	0.1065M	10^{-7}M	0M
Eq.:	$0.1065 - x$	$10^{-7} + x$	x

$K_a = [A^-]_{eq}[H_3O^+]_{eq}/[HA]_{eq} = 1.2\times10^{-6} = (10^{-7}+x)(x)/ 0.1065 - x$

$1.278\times10^{-7} - 1.2\times10^{-6}x = 10^{-7}x + x^2$; $x^2 + 1.3\times10^{-6}x - 1.278\times10^{-7} = 0$

quadratic: $x = 3.56 \times10^{-4}$; $[H_3O^+] = 3.57 \times10^{-4}$; 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 pH=pKa

   Since $K_a = 1.2 \times 10^{-6}$, 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 $[NH_3]/[NH_4^+]$ 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:
   pH= pK_a + log $[NH_3]/[NH_4^+]$; pK_a = -log 5.6 x10^{-10} = 9.25
   pH= 9=9.25 + log $[NH_3]/[NH_4^+]$; $[NH_3]/[NH_4^+]$= 0.56

   b. pH=8.80

   pH= 8.8=9.25 + log $[NH_3]/[NH_4^+]$; $[NH_3]/[NH_4^+]$= 0.35

   c. pH=10.5

   pH= 10.5=9.25 + log $[NH_3]/[NH_4^+]$; $[NH_3]/[NH_4^+]$=17.7

7. A sample of 25 mL of 0.100M NH_3 (K_b= 1.8 x 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

   NH_3 (aq) + H_2O ⇔ NH_4^+(aq) + HO^- (aq)
   Initial: 0.1M 0M 10^{-7}M
   Final: 0.1-x x 10^{-7} + x
   $K_b = [NH_4^+]_{eq}[HO^-]_{eq}/[NH_3]_{eq}$ = (x)(10^{-7} +x) / (0.1-x) = 1.8 x 10^{-5}
   Assume x<<0.1; $10^{-7}x + x^2 = 1.8 \times 10^{-6}$; $x^2 + 10^{-7}x - 1.8\times10^{-6} = 0$
   Quadratic: x=0.00134 (1.3% of 0.1M; 1% is usually the cutoff)
   Solve exactly: $10^{-7}x + x^2 = 1.8 \times 10^{-6} - 1.8 \times 10^{-5}x$;
   $x^2 + 1.81\times10^{-5}x - 1.8 \times10^{-6}$; quadratic x= 0.00133
   $[HO^-]$ = 0.00133 M ; $[H_3O^+]$=7.52x10^{-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!)

   NH_3 (aq) + H_2O ⇔ NH_4^+(aq) + HO^- (aq)
   Initial: 0.0025mol 0M 10^{-7}M
   Final: 0.0017 mol 0.0008 mol
   Final: 0.052 M 0.024M
   pOH = pK_b + log $[NH_4^+]/[NH_3]$ = 4.74 + log (0.024M)/(0.052M) = 4.4
   pH=14-pOH= **9.6**

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

   NH_3 (aq) + H_2O ⇔ NH_4^+(aq) + HO^- (aq)
   Initial: 0.0025mol 0M 10^{-7}M
   Final: 0.0012mol 0.00128mol
   Final: 0.0325 M 0.0341M
   pOH = pK_b + log $[NH_4^+]/[NH_3]$ = 4.74 + log (0.034M)/(0.033M) = 4.76
   pH=14-pOH = **9.24**

d. 25 mL of the 0.10 M HCl to your sample.

NH_3 (aq) + H_2O ⇔ NH_4^+(aq) + HO^- (aq)

Initial:	0.0025mol	0M	10^{-7}M
Final:	0mol	.0025 mol	
Final:	0M	0.05M	

NH_4^+ (aq) + H_2O(l) ⇔ NH_3(aq) + H_3O^+ (aq)

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

$K_a = 5.6 \times 10^{-10} = [NH_3]_{eq}[H_3O^+]_{eq}/[NH_4^+]_{eq} = (x)(10^{-7}+x)/(0.05-x)$

Assume $x \ll 0.05$; $x^2 + 10^{-7}x = 2.8 \times 10^{-11}$; $x^2 + 10^{-7}x - 2.8\times10^{-11}=0$

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

$[H_3O^+] = 10^{-7}+x = 5.34 \times 10^{-6}$; **pH=5.27**