Acid/Base and Titration Problem Set / Answers
Dr. Williamson

1. a) Calculate the amount of 0.1 M H_3PO_4 that it would take to neutralize 100 mL of 0.1 M NaOH.

$$\textbf{0.1M NaOH} = \frac{\textbf{0.1mol NaOH}}{\textbf{1 L NaOH}} * \underline{\textbf{0.1L NaOH}} * \frac{\textbf{1mol OH}^-}{\textbf{1 mol NaOH}} * \frac{\textbf{1mol H}^+}{\textbf{1 mol OH}^-} * \frac{\textbf{1 mol H}_3\textbf{PO}_4}{\textbf{3 mol H}^+} * \frac{\textbf{1L H}_3\textbf{PO}_4}{\textbf{0.1mol H}_3\textbf{PO}_4} =$$

$$= \textbf{0.0333L} = \textbf{33.3 mL}$$

b) Calculate the amount of 0.25 M H_2SO_4 that it would take to neutralize 25 mL of 0.2 M NH_3.

$$\frac{\textbf{0.2mol NH}_3}{\textbf{1 L NH}_3} * \underline{\textbf{0.025L NH}_3} * \frac{\textbf{1mol H}^+}{\textbf{1 mol NH}_3} * \frac{\textbf{1mol H}_2\textbf{SO}_4}{\textbf{2 mol H}^+} * \frac{\textbf{1 L H}_2\textbf{SO}_4}{\textbf{0.25 mol H}_2\textbf{SO}_4} = \textbf{0.01 L} = \textbf{10.0mL}$$

c) Calculate the amount of 0.4 M HCl that it would take to neutralize 20 mL of 0.15 M NaOH.

$$\frac{\textbf{0.15mol NaOH}}{\textbf{1 L NaOH}} * \underline{\textbf{0.02L NaOH}} * \frac{\textbf{1mol H}^+}{\textbf{1 mol NaOH}} * \frac{\textbf{1mol HCl}}{\textbf{1 mol H}^+} * \frac{\textbf{1 L HCl}}{\textbf{0.4 mol HCl}} = \textbf{0.0075 L} = \textbf{7.5 mL}$$

d) Calculate the amount of 0.1 M H_3PO_4 that it would take to neutralize 100 mL of 0.1 M $Ca(OH)_2$.

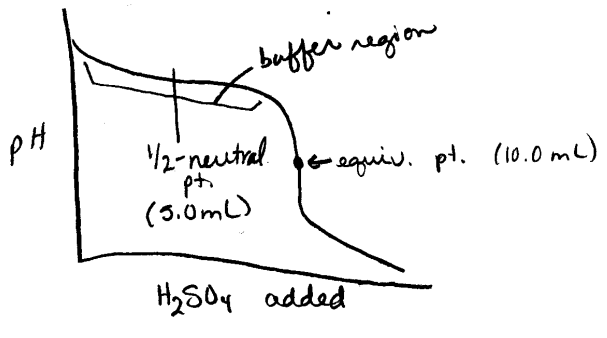
$$\frac{\textbf{0.1mol Ca(OH)}_2}{\textbf{1 L Ca(OH)}_2} * \underline{\textbf{0.1L Ca(OH)}_2} * \frac{\textbf{2mol OH}^-}{\textbf{1 mol Ca(OH)}_2} * \frac{\textbf{1mol H}^+}{\textbf{1 mol OH}^-} * \frac{\textbf{1 mol H}_3\textbf{PO}_4}{\textbf{3 mol H}^+} * \frac{\textbf{1L H}_3\textbf{PO}_4}{\textbf{0.1mol H}_3\textbf{PO}_4} =$$

$$= \textbf{0.0667 L} = \textbf{66.67mL H}_3\textbf{PO}_4$$

2. For the titration of 25 mL of 0.2 M $(CH_3)_3N$, calculate the pH before any 0.25 M H_2SO_4 has been added, the pH when 2.0 mL of H_2SO_4 has been added, the pH 5.0 mL of H_2SO_4 has been added, when 10.0 mL of H_2SO_4 has been added, and when12.0 mL of H_2SO_4 has been added.

① Where is equiv. pt? 10.0 mL H_2SO_4 added

② Where is ½-neutralization? 5.0 mL H_2SO_4 added



<u>no H_2SO_4 added</u>
pH from weak base only

R	$(CH_3)_3N + H_20_{(l)}$	--->	$(CH_3)_3NH^+$	$+ OH^-$
I	0.2M		0	0
C	-x		x	x
E	0.2 –x		x	x

$K_b = 7.4$ e-5 $= x^2/(0.2-x) \approx x^2/(0.2)$ $\quad x = 0.00385 = [OH^-]$
$[OH^-] = 0.00385$
$p[OH] = 2.41 \quad pH = 11.59$

<u>2mL H_2SO_4 added:</u>
So React base and acid first.

R	$2(CH_3)_3N$ +	H_2SO_4 --->	$2(CH_3)_3NH^+$	$+ SO_4^{2-}$
	(.025L) (.2M)	(.002L)(0.25M)		
I	.005	.0005	0	0
C	-.001	-.0005	.001	.0005
F	0.004mol	0	0.001mol	0.0005mol

==> WB + conjugate acidic salt means a Buffer, so use Henderson OR a RICE table
$pOH = pk_b + \log$ [conj acid]/[WB]
= -log (7.4 e-5) + log (.001/.004)* = 3.53
pH = 14-3.53 = 10.47

***need molarity but .001mol/.027L divided by .004mol/.027L is this same as .001/.004**

<u>5.0 mL H_2SO_4 added</u>:
First react base and acid

R	$2(CH_3)_3N$ +	H_2SO_4 --->	$2(CH_3)_3NH^+$	$+ SO_4^{2-}$
	(.025L) (.2M)	(.005L)(0.25M)		
I	.005	.00125mol	0	0
C	-.00250	-.00125	.00250	.00125
F	.0025mol	0	.00250mol	.00125mol

==> 1/2 neutral point so $pOH = pK_b = 4.13$ and pH = 9.87

OR WB + conjugate acidic salt means a Buffer, so use Henderson OR a RICE table
$pOH = pk_b + \log$ [conj acid]/[WB]
= -log (7.4 e-5) + log (.0025mol/.030L divided by .0025mol/.030L)* = 4.13
pH = 14 - 4.13 = 9.87
*** could use (.0025/.0025)**

10.0 mL H_2SO_4 added

First react base and acid

R	**$2(CH_3)_3N$ +**	**H_2SO_4 --->**	**$2(CH_3)_3NH^+$**	**+ SO_4^{2-}**
	(.025L) (.2M)	**(.010L)(0.25M)**		
I	**.005**	**.0025mol**	**0**	**0**
C	**-.005**	**-.0025**	**.005**	**.0025**
F	**0**	**0**	**.005mol**	**.0025mol**

==> Equivalence PT!!!

Find pH of salt.

acidic salt

R	**$(CH_3)_3NH^+ + H_20_{(l)}$ --->**	**$(CH_3)_3N$**	**+ H_3O^+ ↲**
	(.005mol/.035L)		
I	**0.14 M**	**0**	**0**
C	**-x**	**x**	**x**
E	**0.14 –x**	**x**	**x**

$k_a = k_w/k_b = 1\text{ e-}14 / 7.4\text{ e-}5 = 1.35\text{ e-}10 = x^2/(0.14-x) \approx x^2/(0.14)$

$x = 4.35\text{ e-}6 = [H^+]$

pH = 5.36

12.0 mL added

First react base and acid

R	**$2(CH_3)_3N$ +**	**H_2SO_4 --->**	**$2(CH_3)_3NH^+$**	**+ SO_4^{2-}**
	(.025L) (.2M)	**(.012L)(0.25M)**		
I	**.005**	**.003mol**	**0**	**0**
C	**-.005**	**-.0025**	**.005**	**.0025**
F	**0**	**.0005mol**	**.005mol**	**.0025mol**

==> Strong Acid and acidic salt in container ==> pH is from strong acid

.0005mol H_2SO_4 / .037L = .014 M H_2SO_4

strong acid so $[H^+]$ = .028 M

pH = -log .028 M = 1.55

3. Calculate the K_a of the ammonium ion, given that the K_b of NH_3= $1.8x10^{-5}$.

(You may assume 25°C unless otherwise instructed)

at 25°C, $Kw = 1x10^{-14}$

Kw = KaKb (ALWAYS!!!)

$1x10^{-14} = Ka(1.8x10^{-5})$

$Ka = 5.6x10^{-10}$

4. Calculate the pK_b of the fluoride ion given that the pK_a of hydrofluoric acid is $7.2\text{x}10^{-4}$.

    pKa = -log(Ka) ➔ Ka = 10^{-pKa} = $10^{-7.2\ e-4}$ = 0.9983 (don't round quite yet)

    Kw = KaKb = 1.0 x 10^{-14} = 0.9983 Kb ➔ Kb = 1.002 x 10^{-14}

    pKb = -log(Kb) ➔ pKb = 13.9993 ≈ 14

5. Calculate the concentrations of all species present in 0.100 M Oxalic Acid $(COOH)_2$.

    $K_{a1} = 5.9\text{x}10^{-2}$

    $K_{a2} = 6.4\text{x}10^{-5}$

***The first hint that this is a diprotic acid is that you are given 2 Ka's don't differ by 1000 times**

$(COOH)_2 \equiv (COO^-)_2 + H^+$ } Stepwise!!!

<u>First Step</u>:

	HOOCCOOH	$\equiv$	$HOOCCOO^-$	$+ H^+$
I	**0.100**		**0**	**0**
C	**-x**		**+x**	**+x**
E	**0.100-x**		**x**	**x**

(note that hundred times rule fails here… quadratic must be solved)

K_{a1} = x2/(0.100-x) x = {-b ± sqrt(b^2 -4ac) }/2a

x = 0.053 (and an unphysical root)

from step 1

[HOOCCOOH] = 0.100 – 0.053 = 0.047M

[$HOOCCOO^-$] = [H^+] = 0.053M

<u>Second Step</u>:

	$HOOCCOO^-$	$\equiv$	$^-OOCCOO^-$	$+ H^+$	
I	**0.053**		**0**	**0.053**	**notice that there are initial**
C	**-y**		**+y**	**+y**	**concentrations from the first step**
E	**0.053-y**		**y**	**0.053+y**	

(note that hundred times rule fails here… quadratic must be solved)

Notice that the hundred times rule fails here, too… which overcomplicates the problem… so, since
Ka is still relatively small, we will use it, anyway

K_{a2} = (0.053+y)y/(0.053-y) ≈ 0.053y/0.053 = y = 6.4x10^{-5}

[$^-OOCCOO^-$] = y = 6.4x10^{-5}

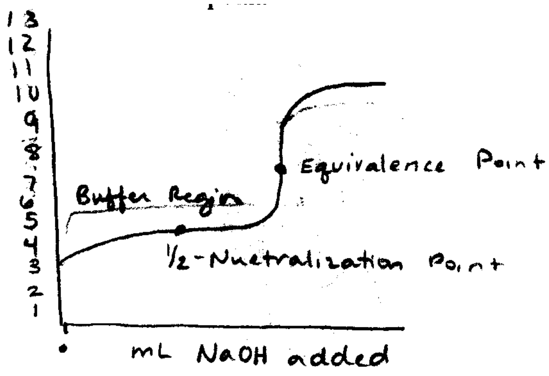
[$HOOCCOO^-$] = 0.053 –y = 0.053 (to 2 sig figs)

[H^+] = 0.053 + y = 0.053 (to 2 sig figs)

[HOOCCOOH] = 0.047M from step 1

pH = -log[H^+] = -log[0.053] = 1.28

6. Sketch the titration curve for a solution of CH_3COOH titrated with NaOH.
   Label the following: Buffer Region, Equivalence Point, the axis (with approximate numbers for the y axis), and Half-neutralization point.



7. Suppose the above titration curve is for 100.0 mL of 0.100 M CH_3COOH titrated with 0.100 M NaOH. Calculate the pH when no NaOH has been added, 20.0 mL NaOH has been added, 50.0 mL NaOH has been added, 75.0 mL NaOH has been added, at equivalence point, and 20.0 mL past equivalence point. (The $K_{a\ \text{acetic acid}} = 1.8\text{x}10^{-5}$)

<u>no NaOH added</u>
pH from weak acid only

R	**$HC_2H_3O_2$**	**<---> H^+**	**+**	**$C_2H_3O_2^-$**	
I	**0.100M**			**0**	**0**
C	**-x**	**x**		**x**	
E	**0.100 –x**	**x**		**x**	

$K_a = 1.8\text{ e-}5 = x^2/(0.100\text{-}x) \approx x^2/(0.100)$ $\quad$ $x = 0.0013 = [H^+]$
pH = 2.87

<u>20mL NaOH added:</u>
So React base and acid first.

R	**$HC_2H_3O_2$ +**	**NaOH**	**--->**	**Na $C_2H_3O_2$ +**	**H_2O *(l)***
	(0.1000L) (.100M)	**(.020L)(0.100M)**			
I	**.010mol**	**.002**		**0**	**0**
C	**-.002**	**-.002**		**.002**	**.002**
F	**0.008mol**	**0**		**0.002mol**	**0.002mol**

==> WA + conjugate basic salt means a Buffer, so use Henderson OR a RICE table
$pH = pk_a + \log [\text{conj base}]/[WA]$
$= -\log (1.8\text{ e-}5) + \log (.002/.008)^* = 4.14$

***need molarity but .002mol/.120L divided by .008mol/.120L is this same as .002/.008**

50.0 mL NaOH added:

First react base and acid

R	$HC_2H_3O_2$	+	NaOH	--->	Na $C_2H_3O_2$ +	H_2O *(l)*
	(0.1000L) (.100M)		(.050L)(0.100M)			
I	.010mol		.0050		0	0
C	-.0050		-.0050	.	0050	.0050
F	0.0050mol		0		0.0050mol	0.0050mol

==> 1/2 neutral point so $pH = pK_a = 4.74$

OR WA + conjugate basic salt means a Buffer, so use Henderson OR a RICE table

$pH = pk_a + \log [\text{conj base}]/[WA]$

$= -\log (1.8\text{ e-}5) + \log (.005\text{mol}/.150\text{L divided by }.005\text{mol}/.150\text{L})^* = 4.74$

* could use (.005/.005)

75.0 mL NaOH added:

First react base and acid

R	$HC_2H_3O_2$	+	NaOH	--->	Na $C_2H_3O_2$ +	H_2O *(l)*
	(0.1000L) (.100M)		(.075L)(0.100M)			
I	.010mol		.0075		0	0
C	-.0075		-.0075	.	0075	.0075
F	0.0025mol		0		0.0075mol	0.0075mol

==> WA + conjugate basic salt means a Buffer, so use Henderson OR a RICE table

$pH = pk_a + \log [\text{conj base}]/[WA]$

$= -\log (1.8\text{ e-}5) + \log (.0075\text{mol}/.175\text{L divided by }.0025\text{mol}/.175\text{L})^* = 5.22$

* could use (.0075/.0025)

At Equivalence Point:

Only salt exists; all acid and base reacted. 0.010 mol of acid; so 0.010 mol of salt

R	$HC_2H_3O_2$	+	NaOH	--->	Na $C_2H_3O_2$ +	H_2O *(l)*
	(0.100L) (.100M)		by def mols needed acid so (.100M)(.100L)			
I	.010mol		0.10		0	
C	-.010		-.010	.	010	
F	0		0		0.010mol	

==> Equivalence PT!!!

Find pH of salt (basic salt)

R	**$C_2H_3O_2^- + H_20_{(l)}$ --->**	**$H C_2H_3O_2$ +**	**OH^-**
	(.010mol/.200L)		
I	**0.05 M**	**0**	**0**
C	**-x**	**x**	**x**
E	**0.05 –x**	**x**	**x**

$k_a = k_w/k_b = 1\ e\text{-}14 / 1.8\ e\text{-}5 = 5.56\ e\text{-}10 = x^2/(0.05\text{-}x) \approx x^2/(0.05)$

$x = 5.3\ e\text{-}6 = [OH^-]$

pOH = 5.28 pH = 14 - 5.28 = 8.72

<u>At 20.0 mL Past Equivalence Point</u>:
First react base and acid

R	**$HC_2H_3O_2$ +**	**NaOH --->**	**Na $C_2H_3O_2$ +**	**H_2O *(l)***
	(0.100L) (.100M)	**(.100M)(.120L)**		
I	**.010mol**	**0.012**	**0**	
C	**-.010**	**-0.010 .**	**010**	
F	**0**	**0.002mol**	**0.010mol**	

==> Strong Base and basic salt in container ==> pH is from strong base

.002 mol NaOH / .220 L = .0091 M NaOH
strong base so $[OH^-]$ = .0091 M
pOH = -log .0091 M = 2.04 pH = 14 – 2.04 = 11.96

Taken from Whitten, Davis, Peck General Chemistry 6th edition

Titration Data for 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

mL 0.100 M NaOH added	mmol Base Added	mmol Excess Acid or Base	pH
0.0	0	10.0 CH_3COOH	2.89
20.0	2	8.00	4.14
50.0	5	5.00	4.74
75.0	7.5	2.50	5.22
90.0	9	1.00	5.7
95.0	9.5	0.50	6.02
99.0	9.9	0.10	6.74
100.0	10	0 (Equivalence Point)	8.72
101.0	10.1	0.1 OH-	10.7
110.0	11	1.00	11.68
120.0	12	2.00	11.96

8. Give the Net Ionic Equations for the following:

$HF_{(aq)} + NaOH_{(aq)} \rightarrow$ **$H_20 + NaF$**

$HF + Na^+ + OH^- \rightarrow H_20 + Na^+ + F^-$

$HF + OH^- \rightarrow H_20 + F^-$

$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow$ **$CH_3COONa + H_2 0$**
$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2 0$
$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2 0$

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow$ **$NaCl + H_2 0$**
$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2 0$
$H^+ + OH^- \rightarrow H_2 0$

2$HCl_{(aq)} + Ca(OH)_{2(aq)} \rightarrow$ **$CaCl2 + 2H_2 0$**
$2H^+ + 2Cl^- + Ca^{2+} + 2OH^- \rightarrow Ca^{2+} + 2Cl^- + 2H_2 0$
$2H^+ + 2OH^- \rightarrow 2H_2 0$

$NH_{3(aq)} + CH_3COOH_{(aq)} \rightarrow$ **$(CH_3COO^-)(NH_4^+)$**
$NH_3 + CH_3COOH \rightarrow CH_3COO^- + NH_4^+$

$NH_{3(aq)} + HCl_{(aq)} \rightarrow$ **NH_4Cl**
$NH_3 + H^+ + Cl^- \rightarrow NH_4^+ + 2Cl^-$
$NH_3 + H^+ \rightarrow NH_4^+$

9. You have 70.0 mL of 0.065 M acetic acid. You then add 0.015 g of Sodium Acetate. You then measure the pH to be 2.2. Calculate $[H^+]$, $[C_2H_3O_2^-]$, and $[HC_2H_3O_2]$ of the final solution.

$[H+] = 10^{-2.2} = 0.0063M$

	$HC_2H_3O_2$ <-->	**H^+ +**	**$C_2H_3O_2^-$**
			[.015g (1mol/ 82.4g)]/ 0.070 L= 0.0026M
I	**0.065**	**0**	**0.0026M (salt)**
C	**-0.0063M**	**+0.0063M**	**+0.0063M**
E	**0.059M**	**0.0063M**	**0.0089M**

$[CH_3COOH] = [CH_3COOH]_o - [CH_3COOH] = 0.065 - 0.0063 = 0.059M$
initial dissociated
=
$[H^+]$

$[CH_3COO^-] = [CH_3COO^-] + [CH_3COO^-]_s = 0.0063 + 0.0026 = 0.0089M$
dissoc. from from salt
CH_3COOH (soluble salt)
=
$[H^+]$

10. Solve (without a calculator):

$\ln(AB) =$ **$\ln(A) + \ln(B)$**

$\ln(A/B) =$ **$\ln(A) - \ln(B)$**

$\ln(AB^N) =$ **$\ln(A) + \ln(B^N) = \ln(A) + N\ln(B)$**

$\ln(1) =$ **0 Think of $\ln(1) = \ln(A/A) = \ln(A) - \ln(A) = 0$**

11. Solve for x (with a calculator if necessary):

$\ln(1/2) = x$	**$x = -0.693$**
$\ln(x) = -5$	**$e^{\ln(x)} = e^{(-5)}$** **$x = e^{(-5)} = 0.0067$**
$-\ln(3x) = 4$	**$-\ln(3x) = 4$** **$e^{\ln(3x)} = e^{(-4)}$** **$3x = e^{(-4)}$** **$x = 1/3\ e^{(-4)} = 0.0061$**