Chapter 12 Homework

1) End Point - Titrant volume corresponding to indicator color change.

Equivalence Point - Titrant volume containing the same number of moles of base as there are acid in the sample solution (or vice versa).

2) 100 mL of 0.100 M NaOH (strong) titrated with 100 M HBr (strong).

$$V_A = 0 \quad \text{pH} = 14 + \log (0.100) = 13$$

$$V_A = 1 \quad \text{moles OH}^- = \frac{0.100 \text{ mmol} \cdot \text{OH}^-}{\text{mL}} \times \frac{100 \text{ mL}}{10.0 \text{ mmol}}$$

$$\text{moles H}^+ = \frac{1.00 \text{ mmol} \cdot \text{H}^+}{\text{mL}} \times \frac{1.00 \text{ mL}}{1.00 \text{ mmol}}$$

$$\begin{align*}
\text{moles OH}^- &= 10.0 - 1.00 = 9.0 \text{ mmol} \\
[\text{OH}^-] &= \frac{9.0 \text{ mmol}}{101 \text{ mL}} = 0.089 \text{ M} \\
\text{pH} &= 14 + \log (0.089) = 12.94
\end{align*}$$
2) \( V_A = 5 \)

\[
[OH^-] = \frac{(10.0 \text{ mmol} - 5.0 \text{ mmol})}{105 \text{ mL}} = 0.0476 \text{ M}
\]

\[
\text{pH} = 14 + \log (0.0476) = 12.68
\]

\( V_A = 9 \)

\[
\text{pH} = 14 + \log \left( \frac{10.0}{10^9} \right) = 11.96
\]

\( V_A = 9.9 \)

\[
\text{pH} = 14 + \log \left( \frac{10.0}{10^{9.9}} \right) = 10.95
\]

\( V_A = 10.0 \)

\[
[OH^-] = \frac{10.0}{10} = 1.0 \text{ M}
\]

\[
\text{pH} = 7.00
\]

\( V_A = 10.1 \)

\[
[OH^-] = \frac{0.1 \text{ mL} \times 1.0 \text{ mmol/mL}}{110.1 \text{ mL}} = 0.000908
\]

\[
\text{pH} = -\log [OH^-] = 2.04
\]

\( V_A = 12.0 \)

\[
[OH^-] = \frac{2.0 \text{ mL} \times 1.0 \text{ mmol/mL}}{112.0} = 0.0176
\]

\[
\text{pH} = -\log (0.0176) = 1.748
\]
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2)

\[ \text{pH} \]

\[ V^{10} \text{acid/mL} \]

3) ON A LINEAR SCALE ON WOULD FIND THAT [OH\(^-\)] SIMPLY FALLS LINEARLY TO ZERO 
(10\(^{-7}\) TO BE EXACT), BUT AS [OH\(^-\)] GOES TO ZERO (OR 10\(^{-7}\))
\( pOH \) GOES TO 7 IN THIS HIGHLY NONLINEAR FASHION!

SPECIFICALLY AS THE LAST OH\(^-\) ARE CONSUMED, THE [OH\(^-\)]
GOES VERY RAPIDLY THROUGH

\[ [OH^-] \quad 0.1 \quad 0.01 \quad 0.001 \quad 0.0001 \quad 0.00001 \quad \text{ETC} \]

\[ \text{pH} \quad 13 \quad 12 \quad 11 \quad 10 \quad 9 \]

BUT TO GO FROM 13 TO 12 IS N.O.1 N.O.1 WHEREAS FROM 10 TO 9 IS 0.0001 N.O.1
SO THE LATTER HAPPENS VERY FAST!
Chapter 12 Homework

4)

\[ \text{pH of Titrant} \]

\[ \text{pK}_A \]

\[ V_{\text{BASE}} \]

\[ V_{\text{EQ}} \]

\[ V_{\text{EQ}/2} \]

**WEAK ACID w/ STRONG BASE**

Within ±1 pH unit of pK\(_A\)

HA + A\(^-\) buffer effectively

So little pH change occurs.

At \( V_{\text{EQ}} \), pH rises rapidly

Towards pH of Titrant

5) **IF ACID IS TOO WEAK, THE**

pK\(_A\) **WILL NOT DIFFER SUBSTANTIALLY FROM THE pH OF TITRANT.**

**IF ACID IS TOO DILUTE BUFFERING CAPACITY WILL BE VERY LOW.**

**BOTH OF THESE WILL MAKE**

\( V_{\text{EQ}} \) **ENDPOINT INDISTINCT.**
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6) \( \text{HA}, \ \text{pK}_a = 5.00, \ \text{V} = 100.0 \text{ mL}, \ 0.100 \text{ M} \)

\text{TITRANT} = 1.00 \text{ M} \ \text{KOH}

\( \text{pH} @ \ \text{V}_B = 0, 1, 5, 9, 9.9, 10, 10.1, 12 \text{ mL} \)

\( \text{V}_B = 0 \)

\[ [\text{HA}] = \frac{\text{H}^+ \text{A}^-}{\text{HA}} = \frac{X^2}{F - X} \approx \frac{X^2}{F} \]

\[ [\text{H}^+] = \sqrt{K_{\text{HA}}} = 0.001 \]

0.001 is much smaller than 0.1, so approx. method justified

\[ \text{pH} = -\log (0.001) = 3.0 \]

\( \text{V}_B = 1 \text{ mL} \)

\[ [\text{HA}] = \frac{(100.0 \text{ mL} \times 0.100 \text{ mmol/L} - (1 \text{ mL} \times 10^{-3} \text{ mmol/L}))}{101.0 \text{ mL}} \]

\[ = \frac{9 \text{ mmol}}{101.0 \text{ mL}} = 0.089 \text{ M} \]

\[ [\text{A}^-] = \frac{1 \text{ mL} \times 1 \text{ mmol/L}}{101 \text{ mL}} = 0.0099 \text{ M} \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{A}^-]}{[\text{H}^+]} \right) = 5.00 - 0.95 = 4.05 \]

\( \text{V}_B = 5 \text{ mL} \)

\[ [\text{HA}] = \frac{10 \text{ mmol} - 5 \text{ mmol}}{105.0 \text{ mL}} = 0.0476 \text{ M} \]

\[ [\text{A}^-] = \frac{5 \text{ mmol}}{105.0 \text{ mL}} = 0.0476 \text{ M} \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{A}^-]}{[\text{H}^+]} \right) = 5.00 \]

\( \text{V}_B = 9 \text{ mL} \)

\[ [\text{HA}] = \frac{10 \text{ mmol} - 9 \text{ mmol}}{109.0 \text{ mL}} = 0.0091 \text{ M} \]

\[ [\text{A}^-] = \frac{1 \text{ mmol}}{109.0 \text{ mL}} = 0.0091 \text{ M} \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{A}^-]}{[\text{H}^+]} \right) = 5.95 \]
CH. 12 HW cont.

6) \( V_B = 9.9 \) ml

\[
\text{pH} = \text{pK_a} + \log \left( \frac{[9.9 \text{ mmol}]}{10.0 - 9.9 \text{ mmol}} \right)
\]

\[
\text{pH} = 6.99
\]

\( V_{12} = 10.0 \) EQ. PT = "pure A-" in 500 mL

\[
[\text{OH}^-] = \sqrt{\frac{K_w \cdot 10.0 \text{ mmol}}{K_a \cdot 110 \text{ mL}}}
\]

\[
[\text{OH}^-] = \sqrt{\frac{10^{-14}}{10^{-5} \cdot 0.909}}
\]

\[
[\text{OH}^-] = 9.5 \times 10^{-6} \text{ (6000 A.M.U., e.e.)}
\]

\[
\text{pH} = 14 - \text{pOH}
\]

\[
\text{pH} = 14 + \log (9.5 \times 10^{-6})
\]

\[
\text{pH} = 8.98
\]

\( V_2 = 10.1 \) ml

\[
[\text{OH}^-] = \frac{0.1 \text{ mmol}}{110.1 \text{ mL}} = 9.08 \times 10^{-5}
\]

\[
\text{pH} = 14 + \log (9.08 \times 10^{-5}) = 10.9
\]

\( V_B = 12 \) ml

\[
\text{pH} = 14 + \log \left( \frac{2 \text{ mmol} \times 1 \text{ mmol}}{112 \text{ mL}} \right)
\]

\[
\text{pH} = 12.3
\]
7) Hydroxyl Acetic Acid, $pK_a = 3.831$

$K_a = 1.48 \times 10^{-5}$

$\text{pH} @ \text{EQ pt.} 0.100\, \text{M HA titrated with} 0.0500\, \text{M KOH}$

1) $C_A V_A = C_B V_B$

$$\frac{V_A}{V_B} = \frac{C_B}{C_A} = \frac{0.0500}{0.100}$$

$$\frac{V_A}{V_0} = 0.5 \quad \text{so} \quad V_T = V_A + V_0$$

$$V_T = V_A + \frac{V_A}{0.5} = 1.5 V_A @ \text{EQ pt}$$

So Hydroxyl Acetate, $[A^-] = \frac{0.100}{1.5} \quad \Rightarrow \quad [A^-] = 0.0667 \, \text{M}$
(cont. 7)  pH of F = 0.0667 M [A⁻]

\[ [A^-] + H_2O = HA + OH^- \]

\[ K_d = \frac{OH^- \cdot HA}{A^-} = \frac{x^2}{F-x} \]

\[ K_B = \frac{K_w}{K_a} = \frac{10^{-14}}{1.44 \times 10^{-4}} = 6.76 \times 10^{-11} \]

Very small so \( x^2 \ll K_B F \) or \( x \approx \sqrt{K_B F} = \sqrt{6.76 \times 10^{-11} \times 0.0667} \)

\[ x \approx 2.1 \times 10^{-6} \text{ M} \approx [OH^-] \]

\[ pH = 14 + \log (2.1 \times 10^{-6}) = 8.32 \]

12)
13) Titration of a weak base $R^-$ with strong acid almost quantitatively produces $13H^+$.

The conjugate acid at the equivalence point, the solution is identical to a solution of pure $BH^+$. Since this is the conjugate acid of $R^-$, it can only donate $H^+$, not accept, so the pH must be $< 7.0$. 

HW CH 12 cont.         9/9