Chem 116 POGIL Worksheet - Week 11 - Solutions
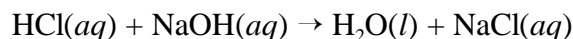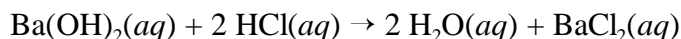## Titration

Key Questions

1. A 25.0-mL sample of 0.100 M HCl(aq) is titrated with 0.125 M NaOH(aq). How many milliliters of the titrant will be need to reach the equivalence point?

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$$

millimol NaOH added = millimol HCl initially present

mL NaOH = (25.0 mL)(0.100 M)/0.125 M = 20.0 mL

2. A 25.0-mL sample of 0.100 M Ba(OH)$_2$(aq) is titrated with 0.125 M HCl(aq). How many milliliters of the titrant will be need to reach the equivalence point?

$$Ba(OH)_2(aq) + 2\ HCl(aq) \rightarrow 2\ H_2O(aq) + BaCl_2(aq)$$

millimol HCl added = 2 × millimol Ba(OH)$_2$ initially present

mL HCl = (2)(25.0 mL)(0.100 M)/0.125 M = 40.0 mL

3. Determine if the pH at the equivalence point is 7, <7, or >7 for the following titrations.
   a. NH$_3$(aq) titrated with HCl(aq)   <7
   b. Ba(OH)$_2$(aq) titrated with HCl(aq)   7
   c. HF(aq) titrated with NaOH(aq)   >7

4. Consider the titration of 25.0 mL of 0.100 M HCl(aq) (the analyte) with 0.0500 M NaOH(aq) (the titrant).

   a. How many milliliters of NaOH(aq) are needed to reach the equivalence point?

   mL NaOH = (25.0 mL)(0.100 M)/0.0500 M = 50.0 mL

   b. How many millimoles of H$_3$O$^+$ are present in the original sample?

   mmol H$_3$O$^+$ = (25.0 mL)(0.100 M) = 2.50 mmol
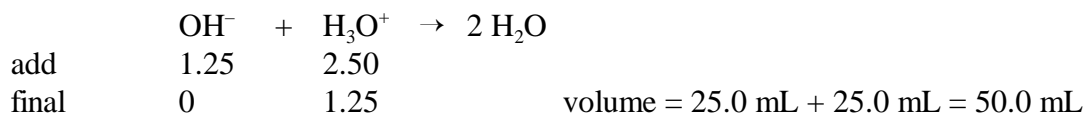
   c. What is the initial pH, before adding any titrant?

   $$[H_3O^+] = C_{HCl} = 0.100\ M$$

   $$pH = -\log(0.100) = 1.000$$

d.   What is the pH after adding 25.0 mL of titrant?

mmol OH^- added = (25.0 mL)(0.0500 M) = 1.25 mmol

	OH^-	+	H_3O^+	→	2 H_2O
add	1.25		2.50		
final	0		1.25		volume = 25.0 mL + 25.0 mL = 50.0 mL

$$[H_3O^+] = 1.25 \text{ mmol}/50.0 \text{ mL} = 2.50 \times 10^{-2} \text{ M}$$
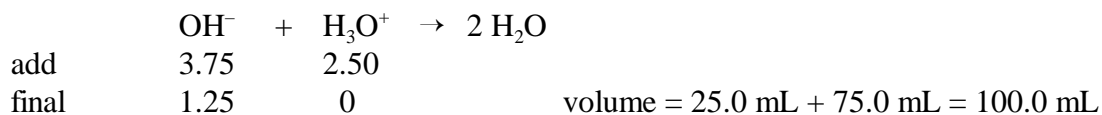
$$pH = 1.602$$

e.   What is the pH after adding 50.0 mL of titrant?

This is the equivalence point (see answer to part a), so pH = 7.000.

f.   What is the pH after adding 75.0 mL of titrant?

mmol OH^- added = (75.0 mL)(0.0500 M) = 3.75 mmol

	OH^-	+	H_3O^+	→	2 H_2O
add	3.75		2.50		
final	1.25		0		volume = 25.0 mL + 75.0 mL = 100.0 mL

$$[OH^-] = 1.25 \text{ mmol}/100.0 \text{ mL} = 1.25 \times 10^{-2} \text{ M}$$

$$pOH = 1.903$$

$$pH = 14.000 - 1.903 = 12.097$$

5. Consider 25.0 mL of 0.100 M HA, for which $K_a = 1.00 \times 10^{-5}$, titrated with 0.0500 M NaOH solution.

a. How many milliliters of NaOH(aq) are needed to reach the equivalence point?

   mL NaOH = (25.0 mL)(0.100 M)/0.0500 M = 50.0 mL

b. How many millimoles of HA are initially present in the sample?

   mmol HA = (25.0 mL)(0.100 M) = 2.50 mmol

c. What is the initial pH, before adding any titrant?

   Before adding any titrant, the solution is pure 0.100 M HA, for which $K_a = 1.0 \times 10^{-5}$. The calculation of pH is identical to the calculation of any other weak acid in pure water. Making our usual assumptions

   $$[H_3O^+] = \sqrt{(0.100)(1.00 \times 10^{-5})} = \sqrt{1.00 \times 10^{-6}} = 1.00 \times 10^{-3} \text{ M}$$

   $$pH = 3.000$$

d. What is the pH after adding 10.0 mL of titrant?

   mmol NaOH added = (10.0 mL)(0.0500 M) = 0.500 mmol

   The net ionic equation and the effect on the amounts of HA and A⁻ are

	HA	+	OH⁻	→	A⁻ +	H₂O
Initial	2.50		0.500		~0	
After rxn	2.00		~0		0.500	

   The total volume at his point is the sum of the initial volume plus the volume of added titrant:
   $$V = 25.0 \text{ mL} + 10.0 \text{ mL} = 35.0 \text{ mL}$$

   Through partial neutralization we have created significant amounts of conjugate base A⁻ and remaining acid HA. The two species are in equilibrium with each other and H_3O^+ and OH⁻ in accord with K_a of HA and K_b of A⁻. We can use either equilibrium expression, but K_a is more convenient at this point, because we are interested in calculating $[H_3O^+]$ and pH. (Of course, we could also use the Henderson-Hasselbalch equation for pH.) At this point we have a buffer solution, and the calculations are identical to that case. As we have seen for buffers, volume is really not important, and therefore we can carry out the calculation using the numbers of millimoles of HA and A⁻.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 1.00 \times 10^{-5} = \frac{[H_3O^+](0.500)}{2.00}$$

$$[H_3O^+] = 2.00 \times 10^{-5}/0.500 = 4.00 \times 10^{-5} \text{ M}$$

$$pH = 4.398$$

Note that for all points after the initial point and before the equivalence point we can ignore volume in the calculations, because at each point in this region we have a buffer. For this reason, this is called the **buffer region** of the titration.

e. What is the pH after adding 25.0 mL of titrant?

$$\text{mmol NaOH added} = (25.0 \text{ mL})(0.0500 \text{ M}) = 1.25 \text{ mmol}$$

This is half way to the equivalence point, called the **half-titration point** or **half-equivalence point.**

	HA	+ OH$^-$	→ A$^-$ + H$_2$O
Initial	2.50	1.25	~0
After rxn	1.25	~0	1.25

At this point we have equal amounts of HA and A$^-$, an equimolar buffer solution. As we have previously seen, whenever $[HA] = [A^-]$, $[H_3O^+] = K_a$ and $pH = pK_a$.. Thus, for this point

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 1.00 \times 10^{-5} = \frac{[H_3O^+](1.25)}{1.25}$$

$$[H_3O^+] = 1.00 \times 10^{-5} \text{ M}$$

$$pH = pK_a = 5.000$$

The half-titration point provides an easy way of estimating the K_a for an unknown weak acid from a titration in which measured pH is followed with added volume of base titrant.

f. What is the pH after adding 50.0 mL of titrant?

This is the equivalence point. At this point, all HA has been converted to A⁻.

	HA	+	OH⁻	→	A⁻	+	H₂O
Initial	2.50		2.50		~0		
After rxn	~0		~0		2.50		
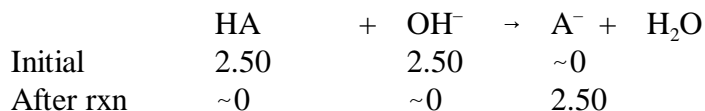
The 2.50 mmol A⁻ is in a volume that is the sum of the initial volume plus the volume of added titrant; i.e., 25.0 mL + 50.0 mL = 75.0 mL. Thus, the analytical concentration of A⁻ is

$$C_{A^-} = \frac{2.50 \text{ mmol}}{75.0 \text{ mL}} = 3.33 \times 10^{-2} \text{ M}$$

The pH of the solution will be governed by the following base hydrolysis equilibrium, which is just the reverse of the neutralization reaction:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$
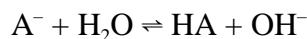
K_b for A⁻, which may be calculated from K_a of HA is

$$K_b = K_w/K_a = 1.00 \times 10^{-14}/1.00 \times 10^{-5} = 1.00 \times 10^{-9}$$

Making the usual assumptions we can calculate [OH⁻] and pOH to obtain pH:

$$[OH^-] = \sqrt{C_A \cdot K_b} = \sqrt{(3.33 \times 10^{-2})(1.00 \times 10^{-9})} = 5.77 \times 10^{-6}$$

$$pOH = 5.239$$

$$pH = 14.000 - 5.239 = 8.761$$

Note that the pH is not 7! For a titration of a weak acid with a strong base titrant, at the equivalence point the pH will always be >7, because we have created a solution of the pure conjugate base in water.

g. What is the pH after adding 75.0 mL of titrant?

This is 25.00 mL beyond equivalence point.

mmol NaOH added = (75.0 mL)(0.0500 M) = 3.75 mmol

	HA	+	OH^-	→	A^-	+	H_2O
Initial	2.50		3.75				
After rxn	~0		1.25		2.50		
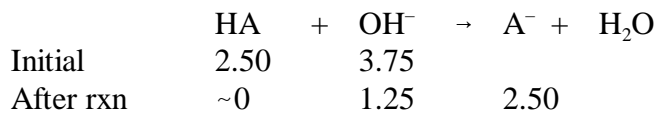
The hydrolysis of A^- supplies so little OH^- that virtually all $[OH^-]$ in this solution is from the excess titrant. The situation is identical to the same point in the preceding example of the strong acid - strong base titration. The total volume at this point is

$$V = 25.0 \text{ mL} + 75.0 \text{ mL} = 100.0 \text{ mL}$$

$$[OH^-] = 1.25 \text{ mmol}/100.0 \text{ mL} = 1.25 \times 10^{-2} \text{ M}$$

$$pOH = 1.903$$

$$pH = 14.000 - 1.903 = 12.097$$

Note that this is the same result we obtained for the previous strong acid titration.