1. Consider the curve shown here for the titration of a weak monoprotic acid with a strong base.



- (a) What is the pH and what is the volume of added base at the equivalence point?
- (b) What is the K_a of the acid?
- (c) If the base was 0.100 M NaOH and 25.00 mL of weak acid was originally titrated, what was the concentration of the original weak acid?

(a): Estimate from graph. pH = 9.0, equivalence point volume = $30.0 \ mL$ of base added. (b): Estimate from graph. $pH = pK_a$ halfway to equivalence point volume. $pK_a = 5.0$, $K_a = 1.0 \times 10^{-5}$ (c): $M_A V_A = M_B V_B \Rightarrow M_A = \frac{M_B V_B}{V_A} = \frac{(0.100 \ M)(30.0 \ mL)}{25.00 \ mL} = 0.12 \ M$

2. Consider the titration of 0.446 g of unknown monoprotic acid with 0.105 M KOH. If 35.00 mL of KOH was required to reach the end point of the titration, what is the molar mass of the acid?

At equivalence point, *mol acid* = *mol base*, so

 $mol \ base = (0.105 \ M)(0.03500 \ L) = 0.003675 \ mol \ base = 0.003675 \ mol \ acid$

Therefore, molar mass $= \frac{0.449 \ g}{0.003675 \ mol} = 121.4 \ g/mol$

Worksheet 8

- 3. Consider the titration of 20.0 mL of 0.105 M acetic acid ($K_a = 1.8 \times 10^{-5}$) with 0.125 M NaOH. Determine each quantity.
 - (a) The initial pH

Initially, we have a weak acid equilibrium:

	$HC_2H_3O_2$	+ H ₂ O	\implies H ₃ O ⁺	+ $C_2H_3O_2^-$
Ι	0.105 M	_	0	0
С	-x	—	+x	+x
Е	0.105 - x	_	x	x
K_a :	$=rac{x^2}{0.105-x}pproxrac{1}{0}$	$\frac{x^2}{0.105} \Rightarrow x =$	$1.37 \times 10^{-3} M$	

Check assumption: $\frac{1.37\times10^{-3}}{0.105}\times100=1.3\%$

$$x = [H_3 O^+] \Rightarrow pH = 2.86$$

(b) The volume of base required to reach the equivalence point

$$M_A V_A = M_B V_B \Rightarrow V_B = \frac{M_A V_A}{M_B} = \frac{(0.105 \ M)(20.0 \ mL)}{0.125 \ M} = 16.8 \ mL \text{ of base added}$$

(c) The pH at 5.0 mL of added base

Reaction: $HA(aq) + OH^{-}(aq) \longrightarrow A^{-}(aq) + H_2O(l)$

Use	moles:						
	$HC_2H_3O_2$	+	OH-	\longrightarrow	$C_2H_3O_2^{-}$	+	H_2O
В	0.0021 mol		0		0		
А	0		0.000625 mol				
Α	0.001475 mol		0		0.000625 mol		

This is a buffer in a new volume of 25.0 mL.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = 4.74 + \log\left(\frac{0.000625 \ mol/25.0mL}{0.001475 \ mol/25.0 \ mL}\right)$$
$$pH = 4.37$$

Note: We have added a little base, so the pH should have increased from the initial pH. But we haven't reached one-half of the equivalence point volume, so pH is a little less than pK_a .

(d) The pH at one-half of the equivalence point

At one-half of the equivalence point volume, $pH = pK_a = 4.74$

(e) The pH at the equivalence point

At the equivalence point, all of the initial moles of weak acid have been converted to weak base (in a new volume of $20.0 \ mL + 16.8 \ mL = 36.8 \ mL$):

	$HC_2H_3O_2$	+	OH-	\longrightarrow	$C_2H_3O_2^{-}$	+	H ₂ O
В	0.0021 mol		0		0		
А	0		0.0021 mol				
А	0 mol		0		0.0021 mol		

Treat as a weak base equilibrium with an initial concentration of $0.0021 \ mol/0.0368 \ L = 0.0571 \ M$:

	$C_2H_3O_2^{-}$	+ H ₂ O	\implies HC ₂ H ₃ O ₂	+ OH ⁻							
Ι	0.0571 M	_	0	0							
С	-x	—	+x	+x							
Е	0.0571 - x	_	Х	Х							
$K_b = \frac{x^2}{0.0571 - x} = 5.56 \times 10^{-10} \approx \frac{x^2}{0.0571}$											
$x = 5.63 \times 10^{-6} M = [OH^{-}] \Rightarrow pOH = 5.25 \Rightarrow pH = 8.75$											

(f) The pH after added 5.0 mL of base beyond the equivalence point

After the equivalence point, any additional volume of base added is in excess of the weak acid. We have added an excess of (0.005 L)(0.125 M) = 0.000625 mol of base. The new volume is 20.0 mL + 16.8 mL + 5.0 mL = 41.8 mL,

giving $[OH^-] = 0.01495 M$

 $pOH = 1.83 \Rightarrow pH = 12.17$

- 4. Consider the titration of 25.0 mL of 0.175 M CH₃NH₂ ($K_b = 4.4 \times 10^{-4}$) with 0.150 M HBr. Determine each quantity.
 - (a) The initial pH

Initially, we have a weak base equilibrium:

	В	+ H ₂ O	<u></u>	BH^+	+	OH ⁻
Ι	0.175 M	_		0		0
С	-x	—		+x		+x
Е	0.175 - x	_		Х		x
$\overline{K_b}$ =	$=\frac{x^2}{0.175-x}=$	4.4×10^{-4}	$\approx \frac{x^2}{0.175}$	$\Rightarrow x =$	0.00	0856 M

(I used successive approximations to solve for x)

$$x = [OH^-] \Rightarrow pOH = 2.07 \Rightarrow pH = 11.93$$

(b) The volume of acid required to reach the equivalence point

$$M_A V_A = M_B V_B$$

$$V_A = \frac{M_B V_B}{M_A} = \frac{(0.175 \ M)(25.0 \ mL)}{0.150 \ M} = 29.2 \ mL$$

(c) The pH at 5.0 mL of added acid

Star	Start with 0.004375 mol B, add 0.00075 mol H_3O^+ .											
	В	+	H_3O^+	\longrightarrow	BH^+	+	H ₂ O					
В	0.004375 mol		0		0							
А	0	0.0)0075 mol									
А	0.003625 mol		0		0.00075 mol							
This	is a buffer, so p	pH = pH	$K_a + log \left(\right)$	$\frac{[B]}{[BH^+]}\bigg) =$	10.64 + log ($\frac{0.0036}{0.000}$	25 mol/30 75 mol/30	$\left(\frac{0.0 \ mL}{0.0mL}\right)$	= 11.32			

Note: This makes sense, we are a little more acidic than the starting point.

(d) The pH at one-half of the equivalence point

 $pH = pK_a = 10.64$

(e) The pH at the equivalence point

Here, all of the initial moles of base have been converted to a weak acid, BH⁺, and the new volume is 25.0 mL + 29.2 mL = 54.2 mL so:

	BH ⁺	+	H ₂ O	<u> </u>	В	+	H_3O^+	_
Ι	0.0807 M		_		0		0	_
С	-x		_		+x		+x	
Е	0.0807 - x		—		x		x	
K_a :	$=\frac{x^2}{0.0807-x}=$	2.29	$\times 10^{-}$	$^{11} \Rightarrow x =$	= 1.3	$6 \times$	$10^{-6} M$	$\Rightarrow pH = 5.8$

Note: This makes sense. We have a weak base, strong acid titration, so the pH should be acidic at the equivalence point.

(f) The pH after added 5.0 mL of acid beyond the equivalence point We have an excess of 0.00075 mol of strong acid in a new volume of 59.2 mL.

 $[H_3O^+] = 0.013 \ M \Rightarrow pH = 1.90$

5. Calculate the molar solubility of Mg(OH)₂ ($K_{sp} = 2.06 \times 10^{-13}$) in pure water.

	$Mg(OH)_2(s)$	+	H ₂ O	<u> </u>	Mg ²⁺	+	2 OH ⁻		
Ι	_		_		0		0		
С	_		_		+S		+2S		
Е	—		-		S		2S		
$\overline{K_{sp}}$	$= [Mg^{2+}][OH]$	-] ² :	= (S)(2	$(S)^2 = ($	$S)(4S^2)$	= 4	S^3		
$S = 3.72 \times 10^{-5} M$									

6. Calculate the molar solubility of Mg(OH)₂ ($K_{sp} = 2.06 \times 10^{-13}$) in *a* solution with pH = 13.00.

This is a common	ion effect pr	oblem. [$[OH^{-}] =$: 0.10 M
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	Mg(OH) ₂ (s)	+	H ₂ O	<u></u>	Mg ²⁺	+	2 OH ⁻
Ι	-		_		0		0.10
С	_		_		+S		+2S
Е	—		—		S		0.10+2S

$$K_{sp} = [Mg^{2+}][OH^{-}]^2 = (S)(0.10 + 2S)^2 \approx (S)(0.10)^2$$

$$S = 2.06 \times 10^{-11} \,\mathrm{M}$$

Note: This is much lower solubility than the previous problem because the OH^- acts as a common ion.