Acid-Base Titrations
CHEM 212

1. Predict the pH at the equivalence point for each of the cases below:

Strong acid/ ~~strong~~ base   weak acid/ strong base   weak base/ strong acid

7   more than 7   less than 7

2. Explain why the pH $\neq$ 7.00 in some cases.

at the equivalence point, the conjugate acid or base is in equilibrium with water.

weak acid / strong base - $BH^+ \rightleftharpoons B + H^+$

weak base / strong acid - $A^- \rightleftharpoons HA + OH^-$

3. Calculate the pH of a solution containing 0.05M weak acid with a pk_a = 5.4. Write the equation for this solution and the equilibrium expression. Use the quadratic equation to solve for $[H^+]$ and calculate the pH

$$HA \rightleftharpoons A^- + H^+ \qquad K_a = \frac{[H^+][A^-]}{[HA]} = 3.98 \times 10^{-6}$$

$$K_a = \frac{x^2}{F-x} \qquad 0 = x^2 + \underset{\uparrow K_a}{3.98 \times 10^{-6}} x - \underset{\uparrow K_a F}{1.99 \times 10^{-7}}$$

$$x = 4.44 \times 10^{-4} \qquad PH = 3.35$$

If $[H^+]$ << F (0.05M), then you can avoid using the quadratic equation to solve the problem. **A good rule of thumb is that you can ignore [H+] in the denominator when [H+] is less than 1% of F.** Use this assumption and rewrite the equilibrium expression. Solve for [H+], and calculate the pH. Do your answers match?

$$K_a = \frac{x^2}{F} \qquad x = 4.46 \times 10^{-4} \qquad pH = 3.35$$

$$x = 0.89\% \, F$$

yes, answers agree if assumption valid

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4. At the equivalence point, mols acid= mols base. Calculate the volume of 0.05 M strong base required to titrate 100 ml of 0.02 M weak acid.

$$0.02 \frac{mol^{HA}}{L} \cdot 0.1 L \cdot \frac{1 \ mol \ OH}{1 \ mol \ HA} \cdot \frac{\cdot L}{0.05 \ mol} \times \frac{1000 \ mL}{L} = 40 mL$$

5. When both species of the conjugate pair are present in solution, it is called a buffer. Buffers are governed by the Henderson- Hasslebach equation. Write the stoichiometry equation and the Henderson Hasslebach equation for both weak acid/strong base and weak base/ strong acid titrations.

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad\qquad B + H^+ \rightleftharpoons BH^+$$
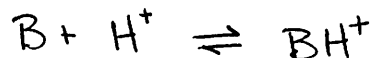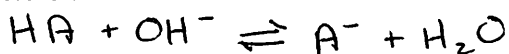
$$pH = pka + \log \frac{[A^-]}{[HA]} \qquad\qquad pH = pK_{BH^+} + \log \frac{[B]}{[BH^+]}$$

6. Determine the pH and volume added at the ½ equivalence volume if the pka= 5.7 for the weak acid above.

$$@ \ \tfrac{1}{2} V_{eq} \quad pH = pka$$

$$volume = \frac{40 mL}{2} = 20 mL$$

7. At the ½ equivalence volume, pH= pka or pH= 14–pkb. Demostrate why this is the case using the Henderson-Hasslebach equation? Then state, in your own words, why this is the case.

$$HA \rightleftharpoons H^+ + A^- \qquad\qquad BH^+ \overset{ka}{\rightleftharpoons} B + H^+$$
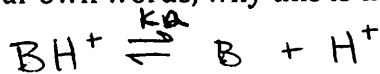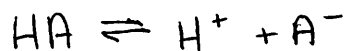
$$pH = pka + 2$$
$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad\qquad K_a = \frac{[H^+][B]}{[BH^+]} \quad \uparrow_{for \ BH^+}$$

$$\log k_a = \log H^+ + \log \frac{[A^-]}{[HA]}$$

$$-\log H^+ = -\log k_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pka + \log \frac{[A^-]}{[HA]} \qquad 2 \qquad pH = pka + \log \frac{[B]}{[BH^+]}$$
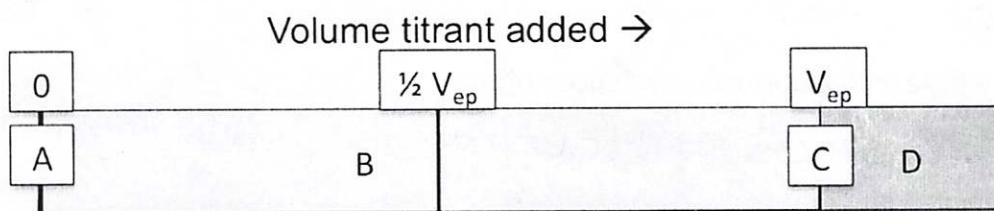
8. For each titration type, write the reactions governing the solution chemistry in each region. Then write the equilibrium expression you would use to calculate the pH.

Volume titrant added →

	0	½ V_{eq}	V_{eq}
A		B B	C D

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad\qquad B + H^+ \rightleftharpoons BH^+$$
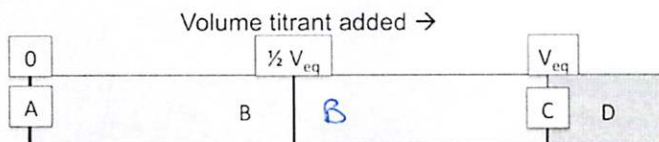
Region	Weak Acid, Strong Base	Weak Base, Strong Acid
A	$HA \overset{Ka}{\rightleftharpoons} H^+ + A^-$ $$k_a = \frac{[H^+][A^-]}{[HA]}$$	$B + H_2O \overset{Kb}{\rightleftharpoons} BH^+ + OH^-$ $$K_b = \frac{[BH^+][OH^-]}{[B]}$$
B	$HA \overset{Ka}{\rightleftharpoons} H^+ + A^-$ $$pH = pka + \log\frac{[A^-]}{[HA]}$$	$B + H^+ \overset{1/Ka}{\rightleftharpoons} BH^+$ $$pH = pk\boxed{a} + \log\frac{[B]}{[BH^+]}$$ ↑ for BH⁺
½ Veq	$pH = pk_a$	$pH = pk_a$
C	$A^- + H_2O \overset{Kb}{\rightleftharpoons} HA + OH^-$ $$K_b = \frac{[HA][OH^-]}{[A^-]}$$	$BH^+ \overset{Ka}{\rightleftharpoons} B + H^+$ $$k_a = \frac{[B][H^+]}{[BH^+]}$$
D	$M_1V_1 = M_2V_2$ $$[OH^-] = [OH_i] \cdot \frac{vol\ excess\ OH^-}{total\ volume}$$ $$pH = 14 - pOH$$	$M_1V_1 = M_2V_2$ $$[H^+] = [H^+_i] \cdot \frac{vol\ excess\ H^+}{total\ volume}$$

9. For a WEAK ACID/STRONG BASE titration, write the reactions governing the solution chemistry in each region. Then write the equilibrium expression you would use to calculate the pH.
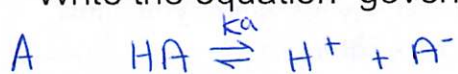
Volume titrant added →

0	½ V_{ep}	V_{ep}
A	B	C D

Write the equation governing the solution chemistry in each region (A-D).

A $\quad HA \overset{ka}{\rightleftharpoons} H^+ + A^- \qquad Ka = \dfrac{[H^+][A^-]}{[HA]}$

B $\quad HA + OH^- \rightleftharpoons A^- + H_2O \qquad pH = pka + \log \dfrac{[A^-]}{[HA]}$

C $\frac{1}{2} V_{eq} \quad pH = pka$

C $\quad A^- + H_2O \overset{Kb}{\rightleftharpoons} HA + OH^- \qquad Kb = \dfrac{Kw}{Ka} = \dfrac{[HA][OH^-]}{[A^-]}$

D $\quad$ ~~moles~~ $\dfrac{excess\ moles\ OH^-}{total\ volume}$
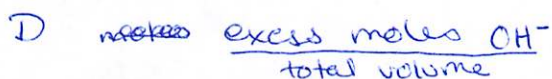
$[H^+] = [OH_i^-] \cdot \dfrac{vol\ excess}{vol\ total}$

10. For a WEAK BASE/STRONG ACID titration, write the reactions governing the solution chemistry in each region. Then write the equilibrium expression you would use to calculate the pH.

Volume titrant added →

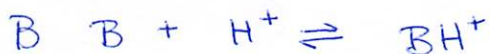| 0	½ V_{ep}	V_{ep}
A	B	C D

Write the equation governing the solution chemistry in each region (A-D).

A $\quad B + H_2O \rightleftharpoons BH^+ + OH^- \qquad Kb = \dfrac{[BH^+][OH^-]}{[B]}$

B $\quad B + H^+ \rightleftharpoons BH^+$

$pH = pka_{\curvearrowright BH^+} + \log \dfrac{[B]}{[BH^+]}$

C $\quad BH^+ \text{ ~~+H₂O~~ } \rightleftharpoons B + H^+$

D $\quad$ ~~~~ $[H^+] = [Titrant] \cdot \dfrac{vol\ added}{vol\ total}$

3
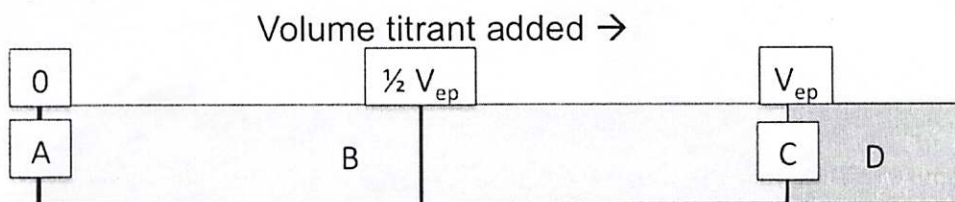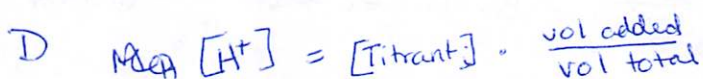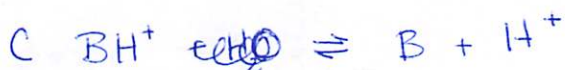
$K_a = 1.995 \times 10^{-6}$

11. A weak acid HA (pKa=5.70) was titrated with 1.00 M KOH. The acid solution had a volume of 100.0 mL and a molarity of 0.100M.

Do you expect the pH at the end point to be greater or less than 7?
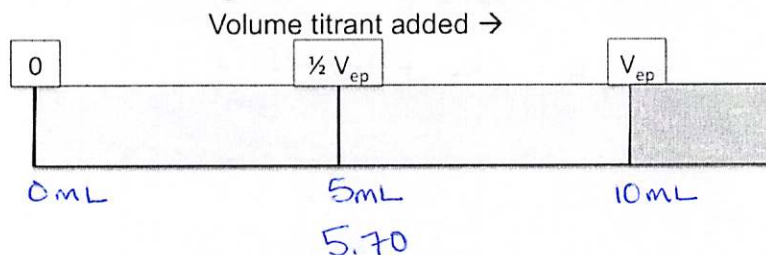
greater than 7

Determine the volume base added at the equivalence point.

$$\frac{0.100 \text{ mol}}{L} \cdot 0.1000 L = 0.01 \text{ moles}$$

moles HA = moles KOH

$$0.01 \text{ moles} \times \frac{L}{1 \text{ mol}} \times 1000 \text{ mL} = 10 \text{ mL KOH}$$

Label this drawing with the locations of the volumes base added and any pH values you know. Refer to this diagram to "check" your calculuations in the rest of the problem.

Volume titrant added →

0	½ V$_{ep}$	V$_{ep}$

0mL   5mL   10mL

5.70

Determin the pH at each of the volumes below. For each case, **begin by writing the equation governing the solution chemistry.**

Before the titration begins.

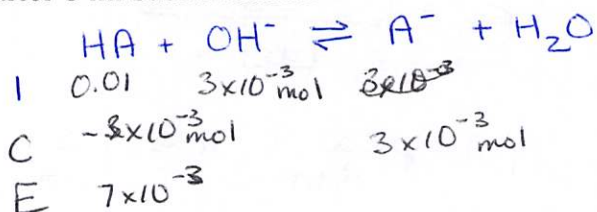$$HA \rightleftharpoons H^+ + A^- \qquad Ka = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x}$$

$x \ll F$

$$F \, Ka = x^2 \rightarrow x = 4.46 \times 10^{-4}$$

$$x = 0.44\% \, F$$

$$pH = 3.35$$

after 3 ml base is added.

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

I	0.01	3×10^{-3} mol	3×10^{-3}
C	-8×10^{-3} mol		3×10^{-3} mol
E	7×10^{-3}		

$$pH = pKa + \log \frac{3 \times 10^{-3}}{7 \times 10^{-3}} = 5.70 \quad \begin{array}{c} +-0.37 \\ +0.4128 \end{array} \quad \begin{array}{c} 5.33 \\ = 6.118 \end{array}$$

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*after 5mL base is added   pH = pka = 5.70

after 7 ml base is added.

$HA + OH^- \rightleftharpoons A^- + H_2O$

I 0.01 7×10^{-3}

C -7×10^{-3} 7×10^{-3}

E 1×10^{-3} 7×10^{-3}
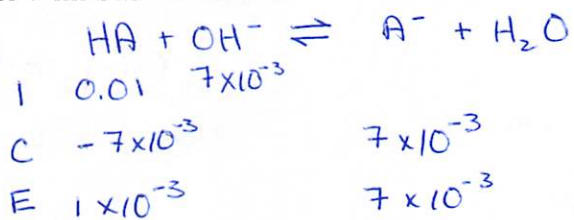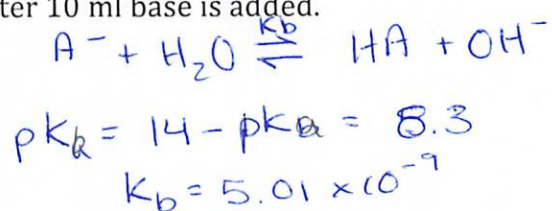
$pH = 5.70 + \log \dfrac{7 \times 10^{-3}}{3 \times 10^{-3}}$

$pH = 5.70 + 0.37 = 6.07$

after 10 ml base is added.

$A^- + H_2O \overset{K_b}{\rightleftharpoons} HA + OH^-$

$pK_b = 14 - pka = 8.3$

$K_b = 5.01 \times 10^{-9}$

assume $X \ll F$

$\sqrt{K_b \cdot F} = x = 2.13 \times 10^{-5} = [OH]$

$x = 0.02\% \cdot F$ $pOH = 4.67$ $pH = 9.32$

$K_b = \dfrac{[HA][OH^-]}{[A^-]} = \dfrac{x^2}{0.01 \text{ moles} - x} = \dfrac{x^2}{0.091 - x}$

$\dfrac{0.01 \text{ moles}}{\dfrac{100 \text{ ml} + 10 \text{ ml}}{1000 \text{ mL}} L}$

after 12 ml base is added.

2 ml excess base

$[OH] = \left(\dfrac{0.002 \, L}{0.112 \, L}\right) \cdot \dfrac{1.00 \, mol}{L} = \cancel{2 \times 10^{-3} M}$ 0.0178 M

$pOH = \cancel{2.69} \, 1.75$

$pH = \cancel{11.300} \, 12.25$

after 15 ml base is added.

5 mL excess base

$[OH] = \left(\dfrac{0.005 L}{0.1015 L}\right) \cdot 1.00 \dfrac{mol}{L} = \cancel{5 \times 10^{-3} M}$ 0.0434 M

$pOH = 1.36$

$pH = 12.67$

$$\text{(benzene ring)}-NH_2 + HCl \rightleftharpoons \text{(benzene ring)}-NH_3^+ + Cl^-$$

12. A 50 ml solution of 0.0319 M benzylamine was titrated with 0.050 M HCl. Given pK_a = ~~543~~
Do you expect the pH at the end point to be greater or less than 7?
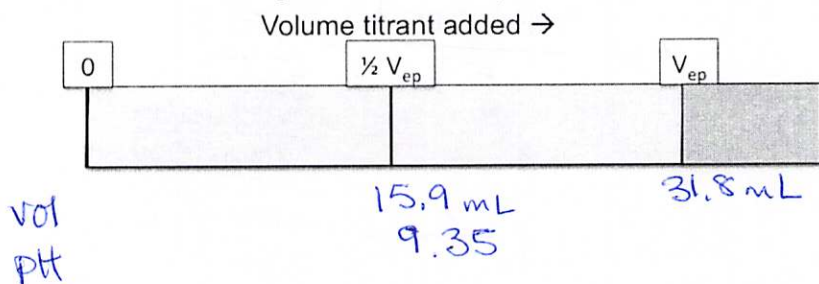
$a = 9.35$

WB/SA   pH < 7

$pK_b = 4.65$

Determine the volume acid added at the equivalence point.

amt base $0.0319 M \cdot 0.05 L = 1.59 \times 10^{-3}$ mol base   monoprotic

@ V_{eq} mol acid = mol base

1.59×10^{-3} mol Acid $\times \dfrac{L}{0.050 mol} \times \dfrac{1000 mL}{L} = 31.8 mL$ acid added @ V_{eq}

Label this drawing with the locations of the volumes base added and any pH values you know.
Refer to this diagram to "check" your calculations in the rest of the problem.

Volume titrant added →

| 0 | ½ V_{ep} | V_{ep} |

vol

$\quad\quad\quad\quad\quad$ 15.9 mL $\quad\quad\quad$ 31.8 mL

pH $\quad\quad\quad\quad\quad$ 9.35

Determin the pH at each of the volumes below. For each case, **begin by writing the equation governing the solution chemistry.**

Before the titration begins.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
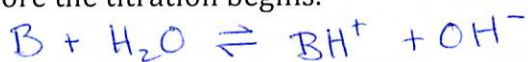
$$K_b = \dfrac{[BH^+][OH^-]}{[B]} = \dfrac{x^2}{F-x} = 2.23 \times 10^{-5}$$

assume $x \ll F$ check assumption $x = 2\% F \rightarrow$ Fail

$$X = \sqrt{K_b F} = 8.45 \times 10^{-4} = [OH^-]$$

$$0 = x^2 + K_b x - F K_b$$

$\quad X = 8.45 \times 10^{-4} M \quad\quad pOH = 3.07$

$pH = 10.926$ ✓

after 6 ml acid is added.

$$B + H^+ \rightleftharpoons BH^+ \quad\quad pH = pK_{BH^+} + \log \dfrac{[B]}{[BH^+]}$$

moles acid added $0.05 \dfrac{mol}{L} \times 0.006 L = 3 \times 10^{-4}$ moles = $[BH^+]$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ total base $\quad\quad\quad$ moles acid added

$$pH = 9.35 + \log \dfrac{1.59 \times 10^{-3} \text{ moles} - 3 \times 10^{-4} \text{ moles}}{3 \times 10^{-4} \text{ moles}} = 9.35 + \log \dfrac{1.29 \times 10^{-3}}{3 \times 10^{-4}}$$

$$pH = 9.35 + 0.633 = 9.98$$

6

after 12 ml acid is added.

$$B + H^+ \rightleftharpoons BH^+ \qquad pH = pk_a + \log \frac{[B]}{[BH^+]}$$

moles acid added $\quad 0.05 \frac{mol}{L} \times 0.012 L = 6 \times 10^{-4}$ moles $= [BH^+]$

$$pH = 9.35 + \log \frac{1.59 \times 10^{-3} \text{ moles} - 6 \times 10^{-4} \text{ moles}}{6 \times 10^{-4} \text{ moles}} = 9.35 + \log 1.65$$
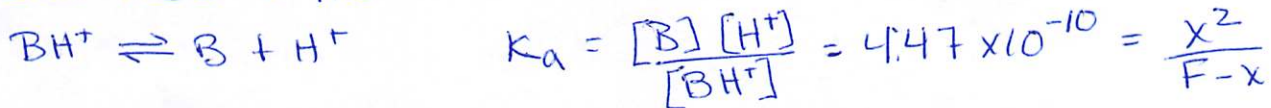
$$pH = 9.567$$

after 16 ml acid is added.

$$\tfrac{1}{2} V_{eq} \Rightarrow pH = pk_a = 9.35$$

after 32 ml acid is added. V_{eq}

moles acid = moles base $= 1.59 \times 10^{-3}$ moles

$$BH^+ \rightleftharpoons B + H^+ \qquad Ka = \frac{[B][H^+]}{[BH^+]} = 4.47 \times 10^{-10} = \frac{x^2}{F - x}$$

$$F = 1.59 \times 10^{-3} \text{ moles} \times \frac{1}{31.8 + 50 \, mL} \times \frac{1000 mL}{L} = 0.0194 \frac{mol}{L}$$

$$x = 2.95 \times 10^{-6} = [H^+]$$

$$pH = 5.53$$

after 35 ml acid is added.

$3.2 \, mL$ excess H^+

$$[H^+] = 0.05 \frac{mol}{L} \cdot \frac{3.2 mL}{85 mL} = 1.88 \times 10^{-3} \, M$$

$$pH = 2.73$$

13. How many grams of NaOH (FM=40 g mol^{-1}) must be added to 1.50 L of a 0.400 M solution of oxoacetic acid ($HCOCO_2H$; pKa=3.46) to produce a buffer pH 4.00?

moles HA + A$^-$ = 1.5L • 0.400 M = 0.6 moles

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

$[OH^-]$ added = $[A^-]$ WA/SB

$$pH = pka + \log \frac{A^-}{HA} \rightarrow 4.0 = 3.46 + \log \frac{A^-}{HA}$$

$$\frac{A^-}{HA} = 3.46$$

$[A^-] = [OH^-]$ added = x

$$\frac{x}{F-x} = 3.46$$

x = 2.076 ̶ 3.46x   x = 0.465 moles

~~x = 3.46 x 0.6 moles~~

~~x moles eOH = 2.0~~

0.465 moles × $\frac{40 g}{mol}$ = 18.62 g

14. A dibasic compound (pK$_{b1}$= 4.00, pK$_{b2}$=8.00) was titrated with 1.00M HCl. The initial solution of B was 0.100M and had a volume of 100 mL. Find the concentration of each species in solution at pH= 6.75.