

$$1. (a) K_b = \frac{[\text{OH}^-][\text{C}_6\text{H}_5\text{NH}_3^+]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$(b) \text{pOH} = -\log[\text{OH}^-]$$

$$5.18 = -\log[\text{OH}^-]$$

$$[\text{OH}^-] = 6.6 \times 10^{-6} M$$

$$[\text{OH}^-] = 6.6 \times 10^{-6} M = [\text{C}_6\text{H}_5\text{NH}_3^+]$$

$$K_b = \frac{[\text{OH}^-][\text{C}_6\text{H}_5\text{NH}_3^+]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(6.6 \times 10^{-6} M)(6.6 \times 10^{-6} M)}{(0.10 M)}$$

$$K_b = 4.4 \times 10^{-10} M$$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 8.82 = 5.18$$

According to the balanced equation above, aniline dissociates into equal concentrations of $\text{C}_6\text{H}_5\text{NH}_3^+$ and OH^- so $[\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{OH}^-]$.

(c) From the definition of molarity, the initial quantity of H^+ and $\text{C}_6\text{H}_5\text{NH}_2$ can be determined as follows:

$$\text{Molarity} = \frac{\# \text{ moles solute}}{\text{L of solution}}$$

$$0.10 M = \frac{\# \text{ moles solute}}{0.0050 \text{ L}}$$

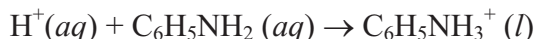
$$\# \text{ moles of solute} = 5.0 \times 10^{-4} \text{ moles}$$

$$\text{Molarity} = \frac{\# \text{ moles solute}}{\text{L of solution}}$$

$$0.10 M = \frac{\# \text{ moles solute}}{0.0250 \text{ L}}$$

$$\# \text{ moles of solute} = 2.5 \times 10^{-3} \text{ moles}$$

The hydrogen ion from the acid will react to aniline as follows:



The reaction will proceed to completion until the limiting reagent is used up. Since there is less hydrogen ion to begin with and it reacts in a 1:1 ratio with the aniline according to the balanced equation, the hydrogen ion is the limiting reagent. The following table summarizes the stoichiometry of the reaction:

	$\text{C}_6\text{H}_5\text{NH}_2$	H^+	$\text{C}_6\text{H}_5\text{NH}_3^+$
Initial	2.5×10^{-3}	5.0×10^{-4}	0
Change	-5.0×10^{-4}	-5.0×10^{-4}	$+5.0 \times 10^{-4}$
Equilibrium	2.0×10^{-3}	0	5.0×10^{-4}

With the addition of the 5.0 mL of HCl, the total volume of the solution is 30.0 mL ($25.0 + 5.0 = 30.0$). So the final concentrations of aniline and its conjugate acid ($\text{C}_6\text{H}_5\text{NH}_3^+$) can be calculated as follows:

$$\text{Molarity} = \frac{\# \text{ moles solute}}{\text{L of solution}}$$

$$\text{Molarity} = \frac{2.0 \times 10^{-3} \text{ moles } \text{C}_6\text{H}_5\text{NH}_2}{0.0300 \text{ L}}$$

$$\text{Molarity} = 0.067 M \text{ C}_6\text{H}_5\text{NH}_2$$

$$\text{Molarity} = \frac{\# \text{ moles solute}}{\text{L of solution}}$$

$$\text{Molarity} = \frac{5.0 \times 10^{-4} \text{ moles } \text{C}_6\text{H}_5\text{NH}_3^+}{0.0300 \text{ L}}$$

$$\text{Molarity} = 0.017 M \text{ C}_6\text{H}_5\text{NH}_3^+$$

$$K_b = 4.4 \times 10^{-10} M = \frac{[\text{OH}^-][\text{C}_6\text{H}_5\text{NH}_3^+]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[\text{OH}^-](0.017 M)}{(0.067 M)} \quad \text{So } [\text{OH}^-] = 1.7 \times 10^{-9} M.$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.7 \times 10^{-9}) = 8.77$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 8.77 = 5.33 = \text{pH}$$

1. (continued)

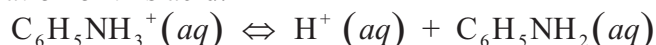
(d) The equivalence point is the point in the titration where enough hydrogen ion (acid) has been added to completely react with all of the base. Since, there was $2.5 \times 10^{-3} M$ of $C_6H_5NH_2$ to before the titration and the mole ratio of aniline to hydrogen ion is 1:1 then the equivalence point occurs when $2.5 \times 10^{-3} M$ of acid is added. The quantities of the participants of the reaction is summarized in the following table:

	$C_6H_5NH_2$	H^+	$C_6H_5NH_3^+$
Initial	2.5×10^{-3}	2.5×10^{-3}	0
Change	-2.5×10^{-3}	-2.5×10^{-3}	$+2.5 \times 10^{-3}$
Equilibrium	0	0	2.5×10^{-3}

The volume of acid added to accumulate $2.5 \times 10^{-3} M$ of H^+ can be calculated from the definition of molarity as shown below. This volume is added to the original volume of aniline to get the total volume of the solution after the titration. This total volume is used to calculate the concentration of $C_6H_5NH_3^+$ at equilibrium as shown below on the right.

$$\begin{aligned} \text{Molarity} &= \frac{\# \text{ moles solute}}{\text{L of solution}} & \text{Molarity} &= \frac{\# \text{ moles solute}}{\text{L of solution}} \\ 0.10 M &= \frac{2.5 \times 10^{-3} \text{ moles of acid}}{\text{L of acid}} & \text{Molarity} &= \frac{2.5 \times 10^{-3} \text{ moles } C_6H_5NH_3^+}{0.0500 \text{ L}} \\ \text{L of acid} &= 2.5 \times 10^{-2} \text{ L} = 25 \text{ mL} & \text{Molarity} &= 0.05 M C_6H_5NH_3^+ \end{aligned}$$

Since $C_6H_5NH_3^+$, a weak acid, is the only major species at equilibrium, the following reaction illustrates the dissociation of this acid.



The K_a for this reaction can be found by dividing the K_w for water by the K_b for the reaction shown above 1. (a) as follows: $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-10}} = 2.3 \times 10^{-5}$. Since $C_6H_5NH_3^+$ dissociates

equally into H^+ and $C_6H_5NH_2$, $[H^+] = [C_6H_5NH_2] = x$.

$$K_a = \frac{[H^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

$$2.3 \times 10^{-5} = \frac{(x)(x)}{0.05}$$

$$x = [H^+] = 1.1 \times 10^{-3} M$$

$$pH = -\log[H^+] = -\log(1.1 \times 10^{-3})$$

pH = 2.96

(e) Erythrosine would be the most suitable indicator for this reaction because it has a pKa (3) value that is closest to the pH (2.96) of the reaction at the equivalence point.

1. (a) $\text{pH} = -\log[\text{H}^+]$
 $4.35 = -\log[\text{H}^+]$

$$\boxed{[\text{H}^+] = 1.1 \times 10^{-5}}$$

(b) $K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]}$

$$2.3 \times 10^{-9} = \frac{(1.8 \times 10^{-5})(1.8 \times 10^{-5})}{[\text{HOBr}]}$$

$$\boxed{\text{HOBr} = 0.14 \text{ M}}$$

- (c) (i) The equivalence point will be reached when the number of moles of OH^- added from the $\text{Ba}(\text{OH})_2$ equals the number of moles of hypobromous acid before titration begins.

HOBr

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{Volume (L) of solution}}$$

$$0.146 \text{ M HOBr} = \frac{\text{number of moles HOBr}}{0.065 \text{ L of solution}}$$

$$\text{number of moles of HOBr} = 0.00949 \text{ moles HOBr}$$

OH^-

$$? \text{ mL Ba}(\text{OH})_2 = 9.5 \times 10^{-3} \text{ moles OH}^- \left(\frac{1 \text{ mole Ba}(\text{OH})_2}{2 \text{ moles OH}^-} \right) \left(\frac{1 \text{ L of Ba}(\text{OH})_2 \text{ solution}}{0.115 \text{ moles Ba}(\text{OH})_2} \right)$$

$$\text{Volume of Ba}(\text{OH})_2 \text{ solution} = 0.041 \text{ L of Ba}(\text{OH})_2 \text{ solution} = \boxed{41 \text{ mL of Ba}(\text{OH})_2 \text{ solution}}$$

- (ii) Greater than 7 because the titration of a weak acid with a strong base produces a basic solution at the equivalence point.

$$\text{OBr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOBr} + \text{OH}^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}} = 4.3 \times 10^{-6}$$

$$4.3 \times 10^{-6} = \frac{[\text{HOBr}][\text{OH}^-]}{[\text{OBr}^-]}$$

$$4.3 \times 10^{-6} = \frac{(x)(x)}{(0.090)}$$

$$x = [\text{OH}^-] = 6.2 \times 10^{-4} \text{ M}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - (-\log[\text{OH}^-]) = 14.00 + \log[6.2 \times 10^{-4} \text{ M}] = 10.79 = \text{pH} > 7$$

(d) $K_a = 2.3 \times 10^{-9} = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]}$

$$2.3 \times 10^{-9} = \frac{(5.00 \times 10^{-9})[\text{OBr}^-]}{0.160}$$

$$[\text{OBr}^-] = \boxed{0.074 \text{ M} = [\text{NaOBr}]}$$
 that must be dissolved

- (e) There are less oxygen atoms, which are very electronegative, in HOBr than HBrO_3 . This means that the electrons are not pulled from the Br atom as much in HOBr than HBrO_3 making the H-Br bond less ionic and harder to ionize in water.

$$3. (a) \% \text{ mass} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 100\% = \left(\frac{0.325 \text{ g}}{2.00 \text{ g}} \right) \times 100\%$$

$$\% \text{ mass} = 16.3\%$$

$$(b) ? \text{ g H} = 1.20 \text{ g H}_2\text{O} \left(\frac{2.00 \text{ g H}}{18.0 \text{ g H}_2\text{O}} \right) = 0.133 \text{ g H}$$

$$PV = nRT$$

$$\left(\frac{750 \text{ mmHg}}{760 \text{ mmHg}} \right) \cdot (3.72 \text{ L}) = n_{\text{CO}_2} (0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}) \cdot (298 \text{ K})$$

$$n_{\text{CO}_2} = 0.150 \text{ mole CO}_2$$

$$? \text{ g C} = 0.150 \text{ mole CO}_2 \left(\frac{12.0 \text{ g C}}{1 \text{ mole CO}_2} \right) = 1.80 \text{ g CO}_2$$

$$m_{\text{C}} + m_{\text{H}} + m_{\text{O}} = m_{\text{Total}}$$

$$1.80 \text{ g} + 0.133 \text{ g} + m_{\text{O}} = 3.00 \text{ g}$$

$$m_{\text{O}} = 1.07 \text{ g}$$

$$m_{\text{C}} = 0.133 \text{ g}$$

$$m_{\text{H}} = 1.80 \text{ g}$$

$$m_{\text{O}} = 1.07 \text{ g}$$

$$(c) \text{ molarity} = \left(\frac{\# \text{ moles of solute}}{L \text{ of solution}} \right)$$

$$0.102 \text{ M NaOH} = \left(\frac{\# \text{ moles of solute}}{0.08843 \text{ L of solution}} \right)$$

$$\# \text{ moles of solute} = 0.00902 \text{ moles NaOH}$$

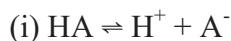


Since the number of moles of OH^- equals the number of moles of H^+ (the mole ratio is 1:1) during neutralization and there is only one ionizable hydrogen, then the number of moles of NaOH equals the number of moles of acetylsalicylic acid.

$$? \text{ g acid} = 1 \text{ mole acid} \left(\frac{1.625 \text{ g acid}}{0.00902 \text{ moles acid}} \right)$$

$$1 \text{ mole acetylsalicylic acid} = 180 \text{ g}$$

$$(d) \text{ molarity} = \left(\frac{\# \text{ moles of solute}}{L \text{ of solution}} \right) = \left(\frac{2.00 \times 10^{-3} \text{ moles}}{0.01500 \text{ L of solution}} \right) = 0.133 \text{ M acetylsalicylic acid}$$



$$\text{pH} = -\log[\text{H}^+]$$

$$2.22 = -\log[\text{H}^+]$$

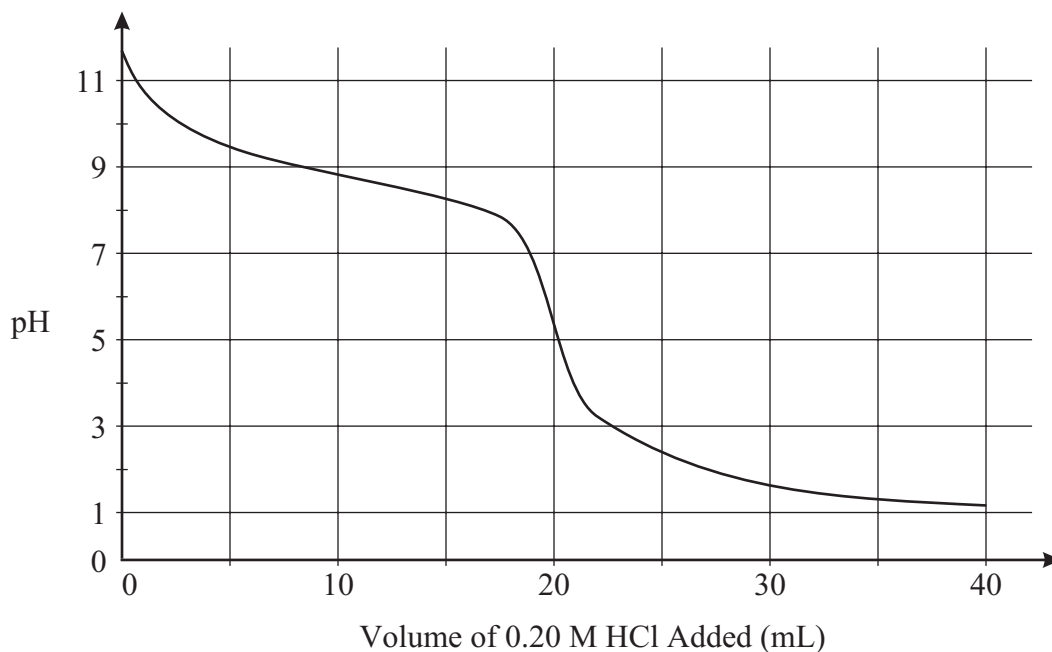
$$[\text{H}^+] = 6.03 \times 10^{-3} \text{ M} = [\text{A}^-]$$

$$[\text{HA}] = 0.133 \text{ M} - 6.03 \times 10^{-3} \text{ M} = 0.127 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.03 \times 10^{-3}) \cdot (6.03 \times 10^{-3})}{0.127} = 2.86 \times 10^{-4} = K_a$$



- (b) See next page for calculations that describe details of graph. These are unnecessary for this test since this section assumes no calculator and only a general form of the graph is necessary here. However, if you are interested, you can look to the next page.



- (c) Methyl Red is the best indicator because its pK_a (5.5) is indicative of an acidic region. The equivalence point from the titration of a weak base with a strong acid will be in the acidic region (below pH of 7). For mathematical details, see the next page (actual equivalence point is 5.26).

- (d) The resulting solution will be basic as shown below.



$$K_a = \frac{K_w}{K_b(\text{for NH}_3)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$[\text{NH}_4^+] = [\text{NH}_3] \quad \text{Therefore } K_a = 5.6 \times 10^{-10} = [\text{H}^+]$$

This will give a pH in the basic region.

$$\text{Mathematical details: } \text{pH} = -\log([\text{H}^+]) = -(\log(5.6 \times 10^{-10})) = 9.25.$$

8. (b) Mathematical Explanations from previous page.

Calculate initial pH (let $x = [\text{OH}^-]$ at equilibrium). $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
Initial	0.10	0	0
Change	$0.10 - x$	x	x
Equilibrium	0.10	1.34×10^{-3}	1.34×10^{-3}

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Since K_b is small, x is small compared to 0.10 M, so $[\text{NH}_3]$ is 0.10 M at equilibrium.**Before Titration:**

$$1.8 \times 10^{-5} = \frac{x \cdot x}{0.10}$$

$$x = 1.34 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(1.34 \times 10^{-3}) = 2.87$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.87 = 11.13$$

Equivalence Point Determination:

$$\text{molarity} = \left(\frac{\text{moles of solute}}{\text{L of solution}} \right)$$

$$0.10 \text{ M NH}_3 = \left(\frac{\# \text{ moles NH}_3}{0.0300 \text{ L solution}} \right)$$

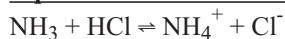
$$\# \text{ moles NH}_3 = 0.0030 \text{ moles NH}_3$$

Therefore, 15 mL HCl solution is the equivalence point of this titration.

$$\text{molarity} = \left(\frac{\text{moles of solute}}{\text{L of solution}} \right)$$

$$0.20 \text{ M HCl} = \left(\frac{0.0030 \text{ moles HCl}}{\# \text{ L solution}} \right)$$

$$\# \text{ L HCl solution} = 0.015 \text{ L HCl solution}$$

Equivalence Point Concentrations:

This reaction goes to completion because ammonia reacts readily with a free proton. Therefore, the number of moles of NH_4^+ = the number of moles HCl added (0.0030 moles) and the concentration of NH_4^+ at the equivalence point (total volume is 40 mL + 15 mL = 55 mL) is:

$$\text{molarity} = \left(\frac{\text{moles of solute}}{\text{L of solution}} \right) = \left(\frac{0.0030 \text{ moles NH}_4^+}{0.055 \text{ L solution}} \right) = 5.5 \times 10^{-2} \text{ M NH}_4^+$$

The dominant equilibrium at the equivalence point is given by: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$

$$K_a = \frac{K_w}{K_b(\text{for NH}_3)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{x \cdot x}{5.5 \times 10^{-2}} \quad \text{let } x = [\text{H}^+]$$

$$x = [\text{H}^+] = 5.55 \times 10^{-6}$$

$$\text{pH} = -\log(5.55 \times 10^{-6}) = 5.26$$

Beyond the Equivalence Point:

Since NH_4^+ is such a weak acid, the main source of H^+ will be excess HCl (after equivalence) which is 25 mL of HCl solution. The total volume of the solution at the end is (40.0 mL + 30.0 mL = 70.0 mL).

$$\text{molarity} = \left(\frac{\text{moles of solute}}{\text{L of solution}} \right)$$

$$\left(\frac{0.005 \text{ moles H}^+}{0.070 \text{ L solution}} \right)$$



$$\text{molarity} = \left(\frac{\text{moles of solute}}{\text{L of solution}} \right) =$$