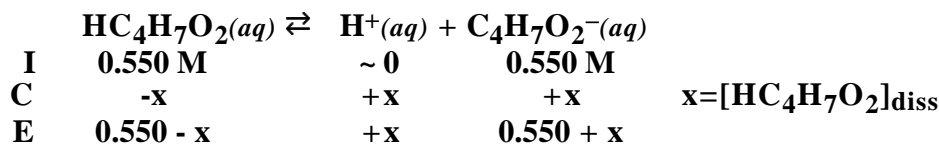


ALL work must be shown in all problems for full credit. **Due at the beginning of class on Wednesday, November 21, 2001**

PS13.1. Determine the pH for a solution containing the following substances[†].

a) 0.550 M HC₄H₇O₂ and 0.550 M NaC₄H₇O₂



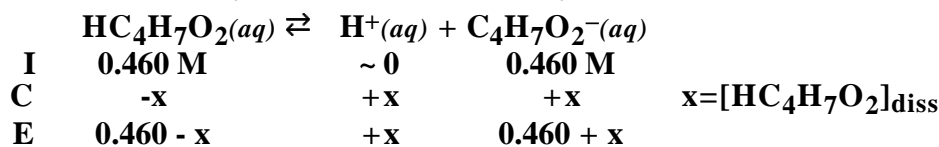
$$K_a = \frac{[\text{C}_4\text{H}_7\text{O}_2^-][\text{H}^+]}{[\text{HC}_4\text{H}_7\text{O}_2]}$$

$$1.5 \times 10^{-5} = \frac{(0.55 + x)(x)}{(0.55 - x)} \quad x < 0.55$$

$$1.5 \times 10^{-5} = \frac{0.55(x)}{0.55}$$

$$1.5 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.82$$

b) 0.460 M HC₄H₇O₂ and 0.460 M NaC₄H₇O₂



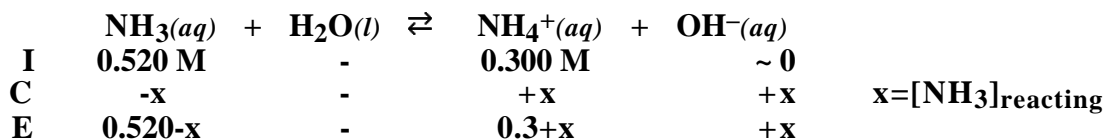
$$K_a = \frac{[\text{C}_4\text{H}_7\text{O}_2^-][\text{H}^+]}{[\text{HC}_4\text{H}_7\text{O}_2]}$$

$$1.5 \times 10^{-5} = \frac{(0.46 + x)(x)}{(0.46 - x)} \quad x < 0.46$$

$$1.5 \times 10^{-5} = \frac{0.46(x)}{0.46}$$

$$1.5 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.82$$

c) 0.300 M NH₄Cl and 0.520 M NH₃



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

$$1.8 \times 10^{-5} = \frac{(0.3 + x)(x)}{0.520 - x} \quad x < .3$$

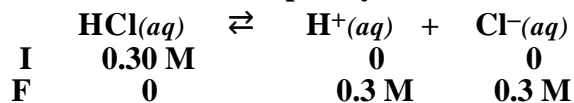
$$1.8 \times 10^{-5} = \frac{(0.3)(x)}{.520}$$

$$3.12 \times 10^{-5} = x = [\text{OH}^-]$$

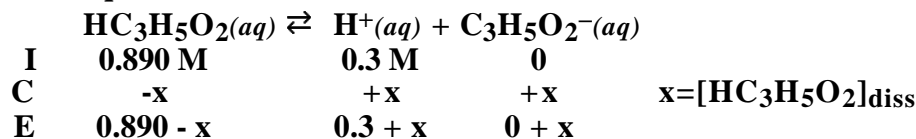
$$\text{pOH} = 4.51 \quad \text{pH} = 9.49$$

d) 0.300 M HCl and 0.890 M HC₃H₅O₂

HCl is a strong acid and it will completely dissociate according to the equation



The H⁺ ion formed from the dissociation of the HCl is used as the initial [H⁺] in the equilibrium reaction.



$$K_a = \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$1.3 \times 10^{-5} = \frac{(0.3 + x)(x)}{(0.890 - x)} \quad x \ll 0.2$$

$$1.3 \times 10^{-5} = \frac{0.3(x)}{0.890}$$

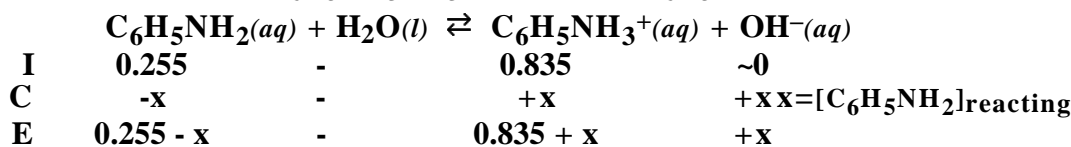
$$3.9 \times 10^{-5} \text{ M} = x$$

$$[\text{H}^+] = 0.3 + x = 0.2 \text{ M} + 3.9 \times 10^{-5} \text{ M} = 0.300 \text{ M}$$

$$\text{pH} = 0.52$$

The amount of H⁺ ion formed from the dissociation of the propionic acid is negligible compared to the amount of hydrogen ion from the HCl.

e) 0.375 M C₆H₅NH₃NO₃ and 0.565 M C₆H₅NH₂



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

$$4.3 \times 10^{-10} = \frac{(0.835 + x)(x)}{0.255 - x} \quad x < .255$$

$$4.3 \times 10^{-10} = \frac{(0.835)(x)}{0.255}$$

$$1.31 \times 10^{-10} = x = [\text{OH}^-]$$

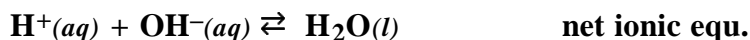
$$\text{pOH} = 9.88 \quad \text{pH} = 4.12$$

Notice because the conjugate acid is stronger (has a larger equilibrium constant) than the base, the solution is acidic!

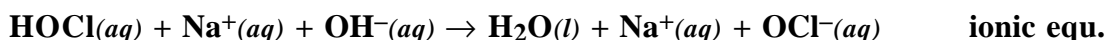
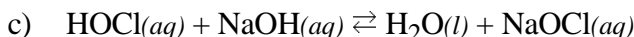
PS13.2. Determine the magnitude of the equilibrium constant for the following reactions



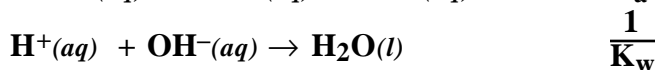
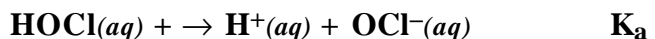
$$K = \frac{1}{[\text{H}^+][\text{OH}^-]} = \frac{1}{K_w} = \frac{1}{1 \times 10^{-14}} = 1 \times 10^{14}$$



$$K = \frac{1}{[\text{H}^+][\text{OH}^-]} = \frac{1}{K_w} = \frac{1}{1 \times 10^{-14}} = 1 \times 10^{14}$$

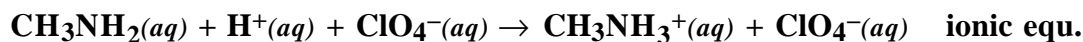


The above ionic equation can be separated into two equations whose K's are known.

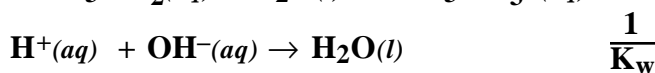


$$K = \frac{K_a(\text{HOCl})}{K_w}$$

$$K = \frac{3.0 \times 10^{-8}}{1.0 \times 10^{-14}} = 3.0 \times 10^6$$



The above ionic equation can be separated into two equations whose K's are known.



$$K = \frac{K_b}{K_w}$$

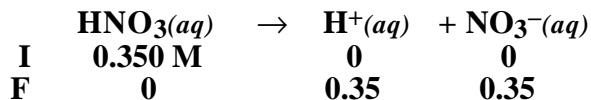
$$K = \frac{4.4 \times 10^{-4}}{1.0 \times 10^{-14}} = 4.4 \times 10^{10}$$

Notice the magnitude for the equilibrium constant for any type of neutralization reaction is very large. Because of the large equilibrium constant, anytime an acid and base are mixed, the reaction proceeds to completion forming the product, salt and water.

PS13.3. A titration is performed by adding 0.250 M KOH to 25.0 mL of 0.350 M HNO₃.

a) Calculate the pH before addition of any KOH.

HNO₃ is a strong acid and it will complete dissociate according to the equation



$$[\text{H}^+] = 0.350 \text{ M}$$

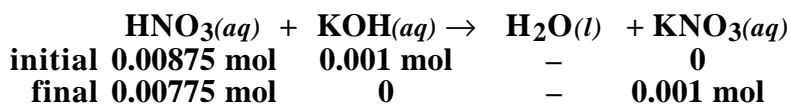
$$\text{pH} = 0.456$$

b) Calculate the pH after the addition of 4.0, 18.0 and 34.0 mL of the base. (Show your work in detail for one of the volumes.)

Add 4.0 mL of 0.250 M KOH

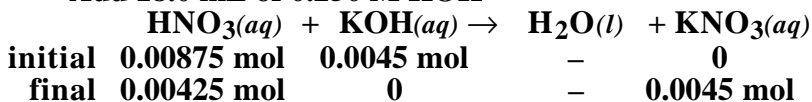
$$4.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.250 \text{ mol}}{1 \text{ L}} \right) = 0.0010 \text{ mol KOH}$$

$$25.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.350 \text{ mol}}{1 \text{ L}} \right) = 0.00875 \text{ mol HNO}_3$$



$$[\text{HNO}_3] = \frac{0.00775 \text{ mol}}{0.029 \text{ L}} = 0.267 \text{ M} \quad \text{pH} = 0.573$$

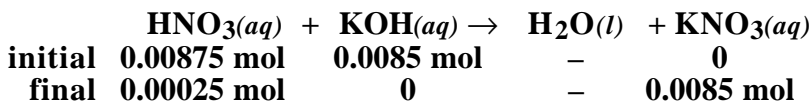
Add 18.0 mL of 0.250 M KOH



$$[\text{HNO}_3] = \frac{0.00425 \text{ mol}}{0.043 \text{ L}} = 9.88 \times 10^{-2} \text{ M}$$

$$\text{pH} = 1.00$$

Add 34.0 mL of 0.250 M KOH



$$[\text{HNO}_3] = \frac{0.00025 \text{ mol}}{0.059 \text{ L}} = 4.24 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.37$$

- c) Calculate the volume of base needed to reach the equivalence point.

At the equivalence point

$$\text{moles}_{\text{acid}} = \text{moles}_{\text{base}}$$

$$\text{moles}_{\text{acid}} \left(\frac{\text{volume}_{\text{acid}}}{\text{volume}_{\text{acid}}} \right) = \text{moles}_{\text{base}} \left(\frac{\text{volume}_{\text{base}}}{\text{volume}_{\text{base}}} \right)$$

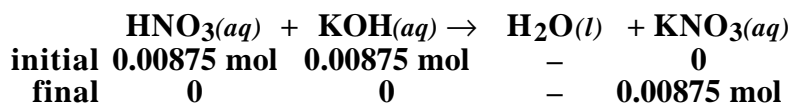
$$M_{\text{acid}} V_{\text{acid}} = M_{\text{base}} V_{\text{base}}$$

$$0.350 \text{ M} \cdot 25.0 \text{ mL} = 0.250 \text{ M} \cdot V_{\text{base}}$$

$$\frac{0.350 \text{ M} \cdot 25.0 \text{ mL}}{0.250 \text{ M}} = V_{\text{base}} = 35.0 \text{ mL}$$

- d) Calculate the pH at the equivalence point.

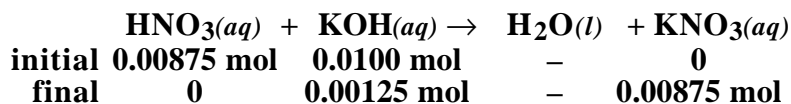
Add 35.0 mL of 0.250 M KOH



KNO_3 is the salt of a strong acid and strong base, so the pH = 7.00 at the equivalence point.

- e) Calculate the pH after adding 5.00 mL of KOH past the endpoint.

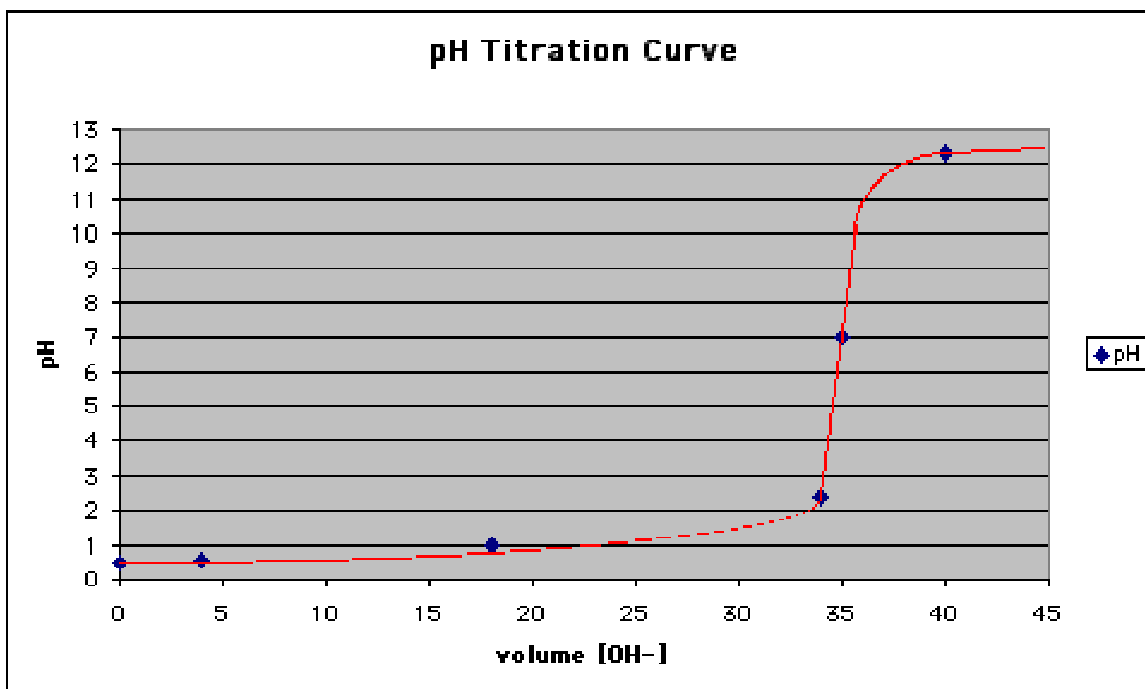
Add 40.0 mL of 0.250 M KOH



$$[\text{KOH}] = \frac{0.00125 \text{ mol}}{0.065 \text{ L}} = 1.92 \times 10^{-2} \text{ M} = [\text{OH}^-]$$

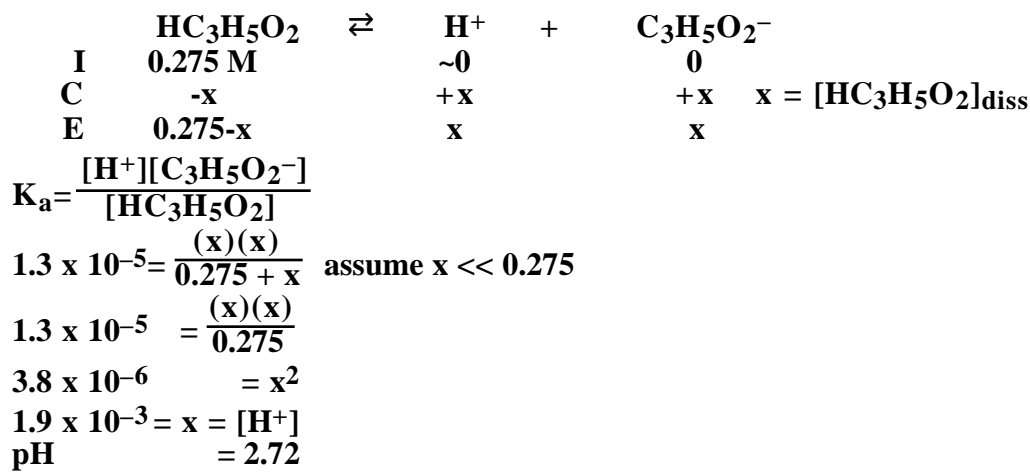
$$\text{pOH} = 1.72 \quad \text{pH} = 12.3$$

- f) Plot pH (y axis) versus volume of KOH added (x axis) for each calculation above. Sketch the titration curve.



PS13.4. A titration is performed by adding 0.200 M NaOH to 30.0 mL of 0.275 M HC₃H₅O₂.

a) Calculate the pH before addition of any NaOH.

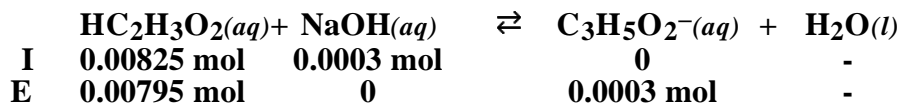


b) Calculate the pH after the addition of 1.5, 20.0, and 40.5 mL of the base. (Show your work in detail for one of the volumes.)

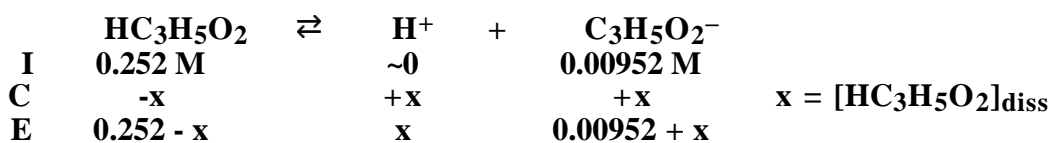
Add 1.5 mL of NaOH

$$[HC_3H_5O_2] = \frac{0.275 \text{ mol}}{L} (0.030 \text{ L}) = 0.00825 \text{ mol}$$

$$[NaOH] = \frac{0.200 \text{ mol}}{L} (0.0015 \text{ L}) = 0.0003 \text{ mol}$$



$$[HC_3H_5O_2] = \frac{0.00795 \text{ mol}}{0.0315 \text{ L}} = 0.252 \text{ M} \quad [C_3H_5O_2^-] = \frac{0.0003 \text{ mol}}{0.0315 \text{ L}} = 0.00952 \text{ M}$$



$$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]}$$

$$1.3 \times 10^{-5} = \frac{(x)(0.00952 + x)}{0.252 - x} \quad \text{assume } x \ll 0.00952$$

$$1.3 \times 10^{-5} = \frac{(x)(0.00952)}{0.252}$$

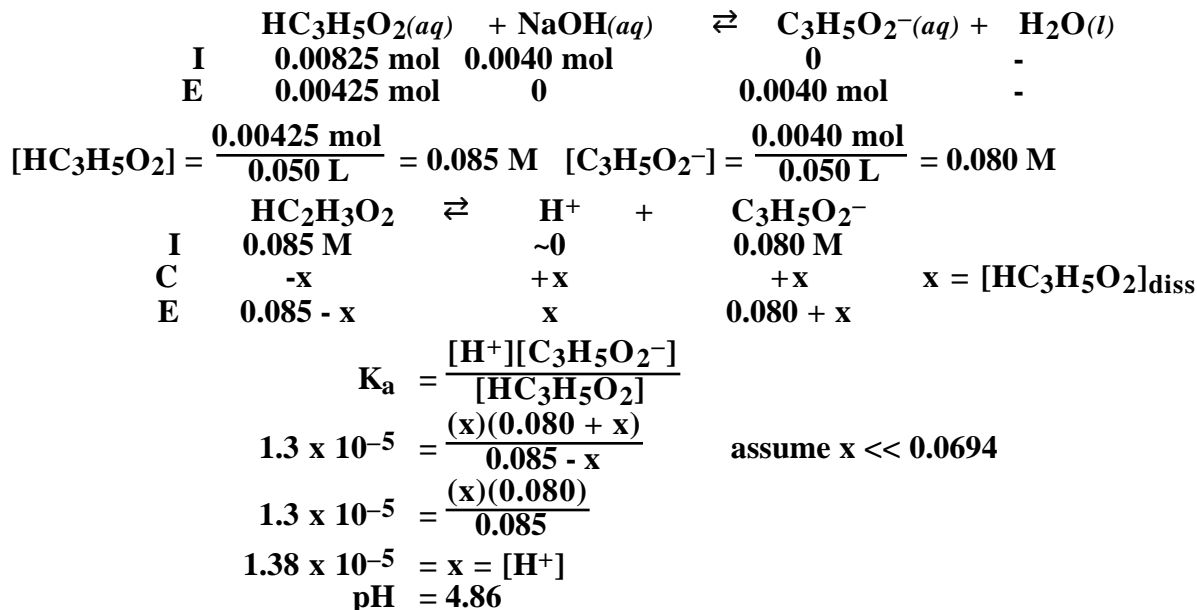
$$3.44 \times 10^{-4} = x = [H^+]$$

pH = 3.46

Add 20.0 mL of NaOH

$$[HC_3H_5O_2] = \frac{0.275 \text{ mol}}{L} (0.030 \text{ L}) = 0.00825 \text{ mol}$$

$$[NaOH] = \frac{0.200 \text{ mol}}{L} (0.020 \text{ L}) = 0.0040 \text{ mol}$$



Add 40.5 mL of NaOH, the pH = 6.62

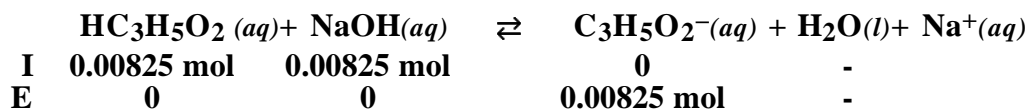
- c) Calculate the volume of base needed to reach the equivalence point.

$$\begin{aligned}
 \text{moles}_{\text{acid}} &= \text{moles}_{\text{base}} \\
 \text{moles}_{\text{acid}} \left(\frac{\text{volume}_{\text{acid}}}{\text{volume}_{\text{acid}}} \right) &= \text{moles}_{\text{base}} \left(\frac{\text{volume}_{\text{base}}}{\text{volume}_{\text{base}}} \right) \\
 M_{\text{acid}} V_{\text{acid}} &= M_{\text{base}} V_{\text{base}} \\
 0.275 \text{ M} \cdot 30.0 \text{ mL} &= 0.200 \text{ M} \cdot V_{\text{base}} \\
 \frac{0.275 \text{ M} \cdot 30.0 \text{ mL}}{0.200 \text{ M}} &= V_{\text{base}} = 41.25 \text{ mL}
 \end{aligned}$$

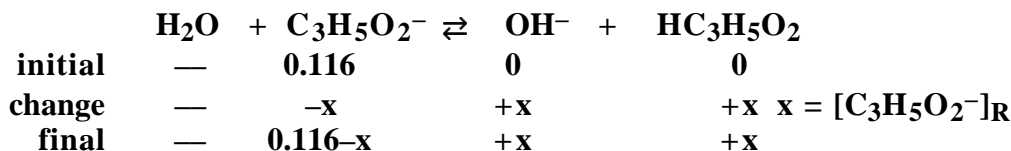
- d) Calculate the pH at the equivalence point.

$$[\text{HC}_3\text{H}_5\text{O}_2] = \frac{0.275 \text{ mol}}{\text{L}} (0.030 \text{ L}) = 0.00825 \text{ mol}$$

$$[\text{NaOH}] = \frac{0.200 \text{ mol}}{\text{L}} (0.04125 \text{ L}) = 0.00825 \text{ mol}$$



$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.00825 \text{ mol}}{0.07125 \text{ L}} = 0.116 \text{ M}$$



$$K_b = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = \frac{[\text{HC}_3\text{H}_5\text{O}_2][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_2^-]}$$

$$7.7 \times 10^{-10} = \frac{[x][x]}{[0.116 - x]} \quad x \ll 0.127$$

$$9.4 \times 10^{-6} = x = [\text{OH}^-]$$

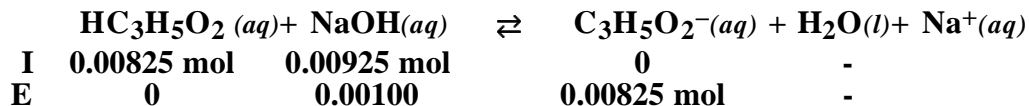
$$\text{pOH} = 5.02 \quad \text{pH} = 8.98$$

e) Calculate the pH after adding 5.00 mL of NaOH past the endpoint.

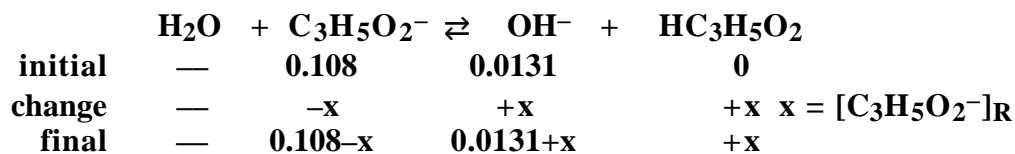
Add 46.25 mL of NaOH

$$[\text{HC}_3\text{H}_5\text{O}_2] = \frac{0.275 \text{ mol}}{\text{L}} (0.030 \text{ L}) = 0.00825 \text{ mol}$$

$$[\text{NaOH}] = \frac{0.200 \text{ mol}}{\text{L}} (0.04625 \text{ L}) = 0.00925 \text{ mol}$$



$$[\text{NaOH}] = \frac{0.0010 \text{ mol}}{0.07625 \text{ L}} = 0.0131 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.00825 \text{ mol}}{0.07625 \text{ L}} = 0.108 \text{ M}$$



$$K_b = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = \frac{[\text{HC}_3\text{H}_5\text{O}_2][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_2^-]}$$

$$7.7 \times 10^{-10} = \frac{[x][.0131 + x]}{[0.108 - x]} \quad x \ll \ll 0.0131$$

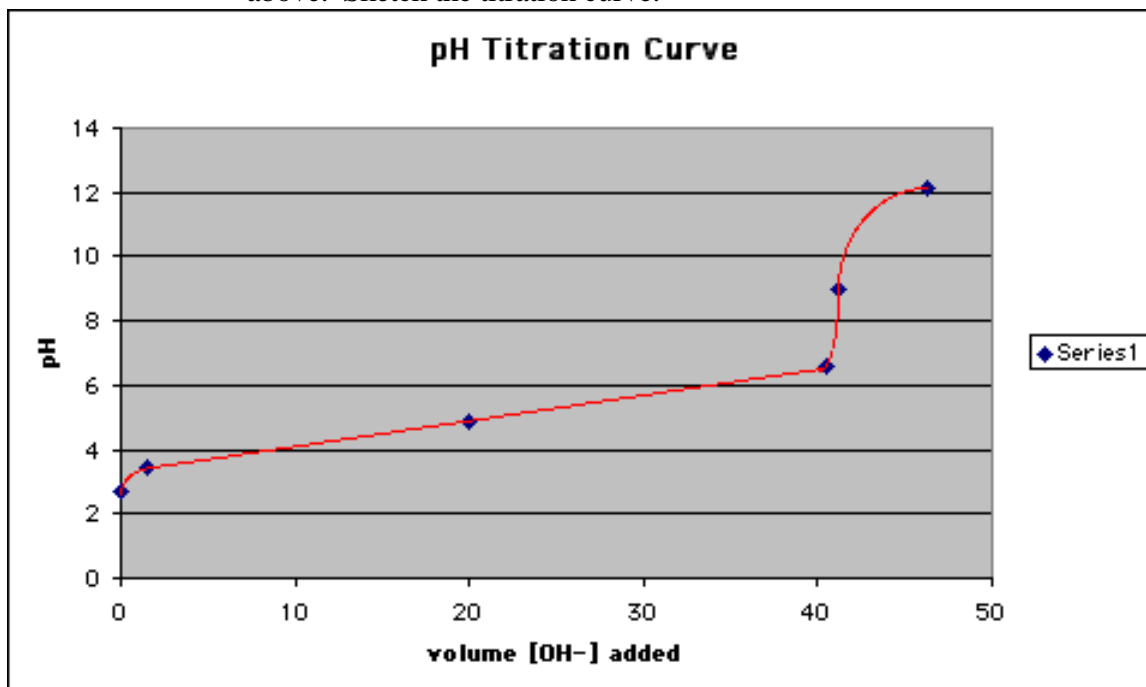
$$6.35 \times 10^{-9} = x$$

$$[\text{OH}^-] = 0.0131 + x$$

$$[\text{OH}^-] = 0.0131 + 6.35 \times 10^{-9} = 0.0131 \text{ M}$$

$$\text{pOH} = 1.88 \text{ and } \text{pH} = 12.1$$

f) Plot pH (y axis) versus volume of NaOH added (x axis) for each calculation above. Sketch the titration curve.



PS13.5. Calculate the pH at the equivalence point when 35.0 mL of 0.160 M ethylamine, CH₃CH₂NH₂, is titrated with 0.120 M HBr

$$M_{\text{acid}}V_{\text{acid}} = M_{\text{base}}V_{\text{base}}$$

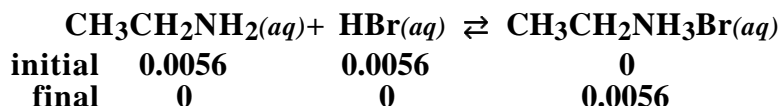
$$0.120 \text{ M} \cdot V_{\text{acid}} = 0.160 \text{ M} \cdot 35.0 \text{ mL}$$

$$V_{\text{acid}} = \frac{0.160 \text{ M} \cdot 35.0 \text{ mL}}{0.120 \text{ M}} = 46.7 \text{ mL}$$

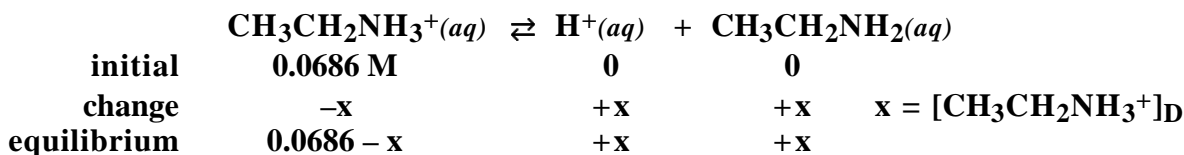
46.7 mL of 0.120 M HBr is needed to reach the end point

$$\text{moles CH}_3\text{CH}_2\text{NH}_2 = \frac{0.160 \text{ mol}}{\text{L}}(0.35 \text{ L}) = 0.0056 \text{ mol}$$

$$\text{moles HBr} = \frac{0.120 \text{ mol}}{\text{L}}(0.0467 \text{ L}) = 0.0056 \text{ mol}$$



$$[\text{CH}_3\text{CH}_2\text{NH}_3] = \frac{0.0056 \text{ mol}}{0.0817 \text{ L}} = 0.0686 \text{ M}$$



$$K_a = \frac{1 \times 10^{-14}}{6.4 \times 10^{-4}} = \frac{[\text{CH}_3\text{CH}_2\text{NH}_2][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{NH}_3^+]}$$

$$1.56 \times 10^{-11} = \frac{[x][x]}{[0.0686 - x]} \quad x \ll 0.0686$$

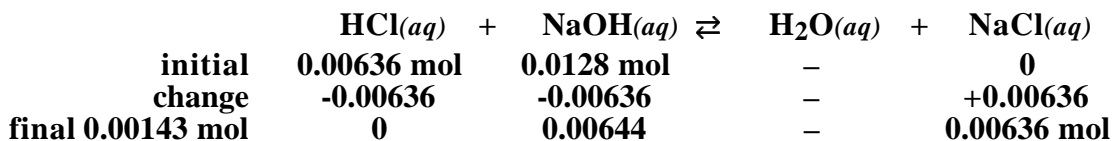
$$1.0 \times 10^{-6} = x = [\text{H}^+]$$

$$\text{pH} = 5.98$$

PS13.6. Calculate the pH of a solution prepared by mixing
 a) 25.0 mL of 0.512 M NaOH and 34.0 mL of 0.187 M HCl

$$\text{moles NaOH} = \frac{0.512 \text{ mol}}{\text{L}}(0.025 \text{ L}) = 0.0128 \text{ mol}$$

$$\text{moles HCl} = \frac{0.187 \text{ mol}}{\text{L}}(0.034 \text{ L}) = 0.00636 \text{ mol}$$



$$[\text{HCl}] = \frac{0.00644 \text{ mol}}{0.059 \text{ L}} = 0.109 \text{ M}$$

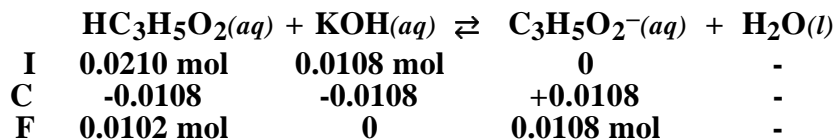
$$\text{pH} = 0.9623$$

PS13.6. (CONTINUED)

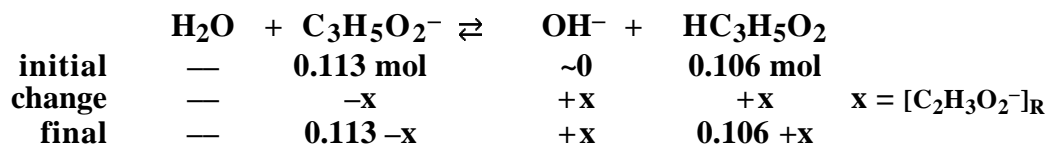
b) 46.0 mL of 0.235 M KOH and 50.0 mL of 0.420 M HC₃H₅O₂

$$\text{moles HC}_3\text{H}_5\text{O}_2 = \frac{0.420 \text{ mol}}{\text{L}}(0.050 \text{ L}) = 0.0210 \text{ mol}$$

$$\text{moles KOH} = \frac{0.235 \text{ mol}}{\text{L}}(0.046 \text{ L}) = 0.0108 \text{ mol}$$



$$[\text{HC}_3\text{H}_5\text{O}_2] = \frac{0.0102 \text{ mol}}{0.096 \text{ L}} = 0.106 \text{ M} \quad [\text{C}_3\text{H}_5\text{O}_2^-] = \frac{0.0108 \text{ mol}}{0.096 \text{ L}} = 0.113 \text{ M}$$



$$K_b = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = \frac{[\text{HC}_3\text{H}_5\text{O}_2][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_2^-]}$$

$$7.69 \times 10^{-10} = \frac{[x][0.106 + x]}{[0.113 - x]} \quad x \ll 0.106$$

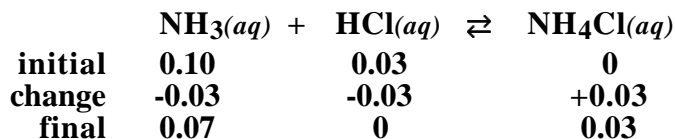
$$8.20 \times 10^{-10} = x = [\text{OH}^-]$$

pOH = 9.09
pH = 4.91

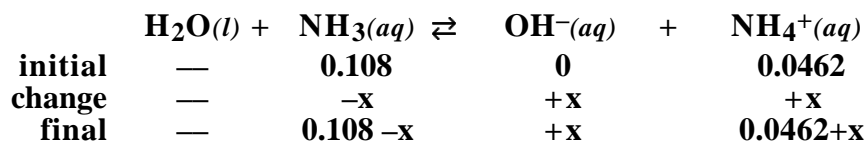
c) 400 mL of 0.250 M NH₃ and 250 mL of 0.120 M HCl

$$\text{moles NH}_3 = \frac{0.250 \text{ mol}}{\text{L}}(0.400 \text{ L}) = 0.100 \text{ mol}$$

$$\text{moles HCl} = \frac{0.120 \text{ mol}}{\text{L}}(0.250 \text{ L}) = 0.0300 \text{ mol}$$



$$[\text{NH}_3] = \frac{0.070 \text{ mol}}{0.650 \text{ L}} = 0.108 \text{ M} \quad [\text{NH}_4^+] = \frac{0.0300 \text{ mol}}{0.650 \text{ L}} = 0.0462 \text{ M}$$



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{[x][0.0462 + x]}{[0.108 - x]} \quad x \ll 0.0154$$

$$4.2 \times 10^{-5} = x = [\text{OH}^-]$$

pOH = 4.38 pH = 9.62