

## Solutions to:

### Acid-Base and Solubility Homework Problem Set

S.E. Van Bramer 1/10/97

1. Calculate the  $\text{H}_3\text{O}^{1+}$  concentration,  $\text{OH}^{1-}$  concentration, pH, and pOH of the following solutions. First solve assuming that  $K_w$  is insignificant. Repeat the calculations and include  $K_w$  (you will need to use the quadratic equation to solve these). When is  $K_w$  significant?

$$M := \text{mole} \cdot \text{liter}^{-1} \quad K_w := 1.0 \cdot 10^{-14} \cdot M^2$$

1-a.  $1.0 \times 10^{-9} \text{ M HNO}_3$

$$C_{\text{acid}} := 1.0 \cdot 10^{-9} \cdot M$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H}_3\text{O}} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}} = 1 \times 10^{-9} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot M^{-1})$$

$$\text{pH} = 9 \quad \text{Does this make sense?}$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 5$$

Assuming  $K_w$  is significant (Included the initial  $[\text{H}_3\text{O}^{1+}]$  in the calculations.)

$$C_{\text{H}_3\text{O}} := \sqrt{K_w} + C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}} = 1.01 \times 10^{-7} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot M^{-1})$$

$$\text{pH} = 6.996$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 7.004$$

1-b.  $1.0 \times 10^{-6} \text{ M HNO}_3$

$$C_{\text{acid}} := 1.0 \cdot 10^{-6} \cdot \text{M}$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H}_3\text{O}^+} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1 \times 10^{-6} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 6$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 8$$

Assuming  $K_w$  is significant (Included the initial  $[\text{H}_3\text{O}^{1+}]$  in the calculations.)

$$C_{\text{H}_3\text{O}^+} := \sqrt{K_w} + C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1.1 \times 10^{-6} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 5.959$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 8.041$$

1-c.  $1.0 \times 10^{-3} \text{ M HNO}_3$

$$C_{\text{acid}} := 1.0 \cdot 10^{-3} \cdot \text{M}$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H}_3\text{O}^+} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1 \times 10^{-3} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 3$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 11$$

Assuming  $K_w$  is significant (Included the initial  $[\text{H}_3\text{O}^{1+}]$  in the calculations.)

$$C_{\text{H}_3\text{O}^+} := \sqrt{K_w} + C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1 \times 10^{-3} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 3$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 11$$

1-d.  $1.0 \times 10^{-1} \text{ M HNO}_3$

$$C_{\text{acid}} := 1.0 \cdot 10^{-1} \cdot \text{M}$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H}_3\text{O}^+} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 0.1 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 1$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 13$$

Assuming  $K_w$  is significant (Included the initial  $[\text{H}_3\text{O}^{1+}]$  in the calculations.)

$$C_{\text{H}_3\text{O}^+} := \sqrt{K_w} + C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 0.1 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 1$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 13$$

1-e.  $1.0 \text{ M HNO}_3$

$$C_{\text{acid}} := 1.0 \cdot \text{M}$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H}_3\text{O}^+} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 0$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 14$$

Assuming  $K_w$  is significant (Included the initial  $[\text{H}_3\text{O}^{1+}]$  in the calculations.)

$$C_{\text{H}_3\text{O}^+} := \sqrt{K_w} + C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}^+} = 1 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = -4.343 \times 10^{-8}$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 14$$

1-f.10.0 M HNO<sub>3</sub>

$$C_{\text{acid}} := 10 \cdot \text{M}$$

Assuming  $K_w$  is insignificant:

$$C_{\text{H3O}} := C_{\text{acid}}$$

$$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$$

$$\text{pOH} := 14 - \text{pH}$$

$$C_{\text{H3O}} = 10 \text{ M}$$

$$\text{pH} = -1$$

$$\text{pOH} = 15$$

*Notice that pH can be negative. At concentrations this high, however, the assumption that all HNO<sub>3</sub> dissociates is probably not accurate.*

Assuming  $K_w$  is significant (Included the initial [H<sub>3</sub>O<sup>1+</sup>] in the calculations.)

$$C_{\text{H3O}} := \sqrt{K_w} + C_{\text{acid}}$$

$$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$$

$$\text{pOH} := 14 - \text{pH}$$

$$C_{\text{H3O}} = 10 \text{ M}$$

$$\text{pH} = -1$$

$$\text{pOH} = 15$$

2. Calculate the H<sub>3</sub>O<sup>1+</sup> concentration, OH<sup>1-</sup> concentration, pH, pOH, nitrate ion concentration and sodium ion concentration for the following experimental steps in a titration. Graph your results.

2-a.6 M HNO<sub>3</sub>.

This is just a strong acid.

$$C_{\text{acid}} := 6 \cdot \text{M}$$

$$C_{\text{H3O}} := C_{\text{acid}}$$

$$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$$

$$\text{pOH} := 14 - \text{pH}$$

$$C_{\text{H3O}} = 6 \text{ M}$$

$$\text{pH} = -0.778$$

$$\text{pOH} = 14.778$$

2-b.Pure Deionized Water.

For pure water, the  $K_w$  equilibrium determines the pH

$$K_w = C_{\text{H3O}} \cdot C_{\text{OH}}$$

$$X := \sqrt{K_w}$$

$$C_{\text{H3O}} := X$$

$$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$$

$$\text{pOH} := 14 - \text{pH}$$

$$C_{\text{H3O}} = X$$

$$C_{\text{OH}} = X$$

$$C_{\text{H3O}} = 1 \times 10^{-7} \text{ M}$$

$$\text{pH} = 7$$

$$\text{pOH} = 7$$

2-c. 1.00 mL of the nitric acid is diluted with deionized water to a volume of 100.0 mL.

The concentration of the acid is :

$$C_{\text{stock}} := 6 \cdot \text{M}$$

$$V_{\text{stock}} := 1.00 \cdot \text{mL}$$

$$V_{\text{acid}} := 100 \cdot \text{mL}$$

$$C_{\text{acid}} := \frac{C_{\text{stock}} \cdot V_{\text{stock}}}{V_{\text{acid}}}$$

$$C_{\text{acid}} = 0.06 \text{ M}$$

The concentrations:

$$C_{\text{H}_3\text{O}} := C_{\text{acid}}$$

$$C_{\text{H}_3\text{O}} = 0.06 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1})$$

$$\text{pH} = 1.222$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 12.778$$

2-d. 5.2468 g of NaOH is dissolved in deionized water to a volume of 1.000 liter.

The concentration of sodium hydroxide is:

$$\text{mass}_{\text{base}} := 5.2468 \cdot \text{gm}$$

$$\text{MW}_{\text{base}} := (22.990 + 15.999 + 1.0079) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{\text{base}} := \frac{\text{mass}_{\text{base}}}{\text{MW}_{\text{base}}}$$

$$\text{volume}_{\text{base}} := 1000 \cdot \text{mL}$$

$$C_{\text{base}} := \frac{\text{mole}_{\text{base}}}{\text{volume}_{\text{base}}}$$

$$C_{\text{base}} = 0.1312 \text{ M}$$

The concentrations:

$$C_{\text{OH}} := C_{\text{base}}$$

$$C_{\text{OH}} = 0.131 \text{ M}$$

$$\text{pOH} := -\log(C_{\text{base}} \cdot \text{M}^{-1})$$

$$\text{pOH} = 0.882$$

$$\text{pH} := 14 - \text{pOH}$$

$$\text{pH} = 13.118$$

2-e.0.100 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 0.1 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 100.1 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O already present.

$$\text{mole}_{\text{H}_3\text{O}} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}} \quad \text{mole}_{\text{H}_3\text{O}} = 5.987 \times 10^{-3} \text{ mole}$$

$$C_{\text{H}_3\text{O}} := \frac{\text{mole}_{\text{H}_3\text{O}}}{V_{\text{total}}} \quad C_{\text{H}_3\text{O}} = 0.06 \text{ M}$$

$$C_{\text{OH}} := \frac{K_w}{C_{\text{H}_3\text{O}}} \quad C_{\text{OH}} = 1.672 \times 10^{-13} \text{ M}$$

$$\text{pH} := -1 \cdot \log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) \quad \text{pH} = 1.223$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 12.777$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \quad C_{\text{NO}_3} = 0.06 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \quad C_{\text{Na}} = 1.31 \times 10^{-4} \text{ M}$$

2-f. 1.00 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 1.00 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 101 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O<sup>+</sup> already present.

$$\text{mole}_{\text{H}_3\text{O}^+} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}} \quad \text{mole}_{\text{H}_3\text{O}^+} = 5.869 \times 10^{-3} \text{ mole}$$

$$C_{\text{H}_3\text{O}^+} := \frac{\text{mole}_{\text{H}_3\text{O}^+}}{V_{\text{total}}} \quad C_{\text{H}_3\text{O}^+} = 0.058 \text{ M}$$

$$C_{\text{OH}^-} := \frac{K_w}{C_{\text{H}_3\text{O}^+}} \quad C_{\text{OH}^-} = 1.721 \times 10^{-13} \text{ M}$$

$$\text{pH} := -1 \cdot \log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1}) \quad \text{pH} = 1.236$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 12.764$$

$$C_{\text{NO}_3^-} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \quad C_{\text{NO}_3^-} = 0.059 \text{ M}$$

$$C_{\text{Na}^+} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \quad C_{\text{Na}^+} = 1.299 \times 10^{-3} \text{ M}$$

2-g. 10.00 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 10.00 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 110 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O already present.

$$\text{mole}_{\text{H}_3\text{O}} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}} \quad \text{mole}_{\text{H}_3\text{O}} = 4.688 \times 10^{-3} \text{ mole}$$

$$C_{\text{H}_3\text{O}} := \frac{\text{mole}_{\text{H}_3\text{O}}}{V_{\text{total}}} \quad C_{\text{H}_3\text{O}} = 0.043 \text{ M}$$

$$C_{\text{OH}} := \frac{K_w}{C_{\text{H}_3\text{O}}} \quad C_{\text{OH}} = 2.346 \times 10^{-13} \text{ M}$$

$$\text{pH} := -1 \cdot \log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) \quad \text{pH} = 1.37$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 12.63$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \quad C_{\text{NO}_3} = 0.055 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \quad C_{\text{Na}} = 0.012 \text{ M}$$

2-h.20.00 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 20 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 120 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O already present.

$$\text{mole}_{\text{H}_3\text{O}} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}} \quad \text{mole}_{\text{H}_3\text{O}} = 3.376 \times 10^{-3} \text{ mole}$$

$$C_{\text{H}_3\text{O}} := \frac{\text{mole}_{\text{H}_3\text{O}}}{V_{\text{total}}} \quad C_{\text{H}_3\text{O}} = 0.028 \text{ M}$$

$$C_{\text{OH}} := \frac{K_w}{C_{\text{H}_3\text{O}}} \quad C_{\text{OH}} = 3.554 \times 10^{-13} \text{ M}$$

$$\text{pH} := -1 \cdot \log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) \quad \text{pH} = 1.551$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 12.449$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \quad C_{\text{NO}_3} = 0.05 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \quad C_{\text{Na}} = 0.022 \text{ M}$$

2-i. Enough sodium hydroxide solution is added to reach the equivalence point.

At the equivalence point enough base is added so that the moles of hydroxide and the moles of nitric acid are equivalent.

$$\text{mole}_{\text{acid}} := C_{\text{acid}} \cdot V_{\text{acid}} \qquad \text{mole}_{\text{acid}} = 6 \times 10^{-3} \text{ mole}$$

$$\text{mole}_{\text{base}} := \text{mole}_{\text{acid}} \qquad \text{mole}_{\text{base}} = 6 \times 10^{-3} \text{ mole}$$

$$V_{\text{base}} := \frac{\text{mole}_{\text{base}}}{C_{\text{base}}} \qquad V_{\text{base}} = 45.739 \text{ mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}} \qquad V_{\text{total}} = 145.739 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O already present.

$$\text{mole}_{\text{H}_3\text{O}} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}} \qquad \text{mole}_{\text{H}_3\text{O}} = 0 \text{ mole}$$

Since the acid and base do not contribute to the pH, it is the same as pure water:

For pure water, the  $K_w$  equilibrium determines the pH

$$K_w = C_{\text{H}_3\text{O}} \cdot C_{\text{OH}} \qquad C_{\text{H}_3\text{O}} = X \qquad C_{\text{OH}} = X$$

$$X := \sqrt{K_w}$$

$$C_{\text{H}_3\text{O}} := X \qquad C_{\text{H}_3\text{O}} = 1 \times 10^{-7} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) \qquad \text{pH} = 7$$

$$\text{pOH} := 14 - \text{pH} \qquad \text{pOH} = 7$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \qquad C_{\text{NO}_3} = 0.041 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \qquad C_{\text{Na}} = 0.041 \text{ M}$$

2-j. 50.00 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 50 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 150 \text{ mL}$$

Calculate the pH by assuming that all the added OH<sup>-</sup>, reacts with H<sub>3</sub>O already present.

$$\text{mole}_{\text{H}_3\text{O}} := C_{\text{acid}} \cdot V_{\text{acid}} - C_{\text{base}} \cdot V_{\text{base}}$$

$$\text{mole}_{\text{H}_3\text{O}} = -5.59 \times 10^{-4} \text{ mole}$$

*This result does not make any sense because nitric acid is now the limiting reagent. So OH<sup>1-</sup> is in excess and determines the pH*

$$\text{mole}_{\text{OH}} := C_{\text{base}} \cdot V_{\text{base}} - C_{\text{acid}} \cdot V_{\text{acid}}$$

$$\text{mole}_{\text{OH}} = 5.59 \times 10^{-4} \text{ mole}$$

$$C_{\text{OH}} := \frac{\text{mole}_{\text{OH}}}{V_{\text{total}}}$$

$$C_{\text{OH}} = 3.727 \times 10^{-3} \text{ M}$$

$$\text{pOH} := -\log(C_{\text{OH}} \cdot \text{M}^{-1})$$

$$\text{pOH} = 2.429$$

$$\text{pH} := 14.0 - \text{pOH}$$

$$\text{pH} = 11.571$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}}$$

$$C_{\text{NO}_3} = 0.04 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}}$$

$$C_{\text{Na}} = 0.044 \text{ M}$$

2-k. 100.0 mL of the sodium hydroxide solution is added to the nitric acid solution.

$$V_{\text{acid}} := 100 \cdot \text{mL} \quad V_{\text{base}} := 100 \cdot \text{mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{base}}$$

$$V_{\text{total}} = 200 \text{ mL}$$

$$\text{mole}_{\text{OH}} := C_{\text{base}} \cdot V_{\text{base}} - C_{\text{acid}} \cdot V_{\text{acid}} \quad \text{mole}_{\text{OH}} = 7.118 \times 10^{-3} \text{ mole}$$

$$C_{\text{OH}} := \frac{\text{mole}_{\text{OH}}}{V_{\text{total}}} \quad C_{\text{OH}} = 0.036 \text{ M}$$

$$\text{pOH} := -\log(C_{\text{OH}} \cdot \text{M}^{-1}) \quad \text{pOH} = 1.449$$

$$\text{pH} := 14.0 - \text{pOH} \quad \text{pH} = 12.551$$

$$C_{\text{NO}_3} := \frac{C_{\text{acid}} \cdot V_{\text{acid}}}{V_{\text{total}}} \quad C_{\text{NO}_3} = 0.03 \text{ M}$$

$$C_{\text{Na}} := \frac{C_{\text{base}} \cdot V_{\text{base}}}{V_{\text{total}}} \quad C_{\text{Na}} = 0.066 \text{ M}$$

3. What is the pH and pOH of a buffer prepared by adding 1.2435 g of sodium acetate to 100 mL of 0.124 M acetic acid. Calculate using the Henderson-Hasselbalch equation (as shown in your textbook) and using the quadratic equation (as shown in class).

$$K_a := 1.8 \cdot 10^{-5} \cdot M$$

The concentration of the acid in the buffer is:

$$C_{\text{acid}} := 0.124 \cdot M$$

The concentration of the salt is (Fill in appropriate values and delete unnecessary sections.):

$$\text{mass}_{\text{salt}} := 1.2435 \cdot \text{gm}$$

$$\text{MW}_{\text{salt}} := [(22.990) + (2 \cdot 12.001) + (3 \cdot 1.0079)] + (2 \cdot 15.999) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{\text{salt}} := \frac{\text{mass}_{\text{salt}}}{\text{MW}_{\text{salt}}} \quad \text{mole}_{\text{salt}} = 0.015 \text{ mole}$$

$$V_{\text{salt}} := 100 \cdot \text{mL}$$

$$C_{\text{salt}} := \frac{\text{mole}_{\text{salt}}}{V_{\text{salt}}} \quad C_{\text{salt}} = 0.152 \text{ M}$$

The equilibrium solution for	HA	+	H <sub>2</sub> O	<->	H <sub>3</sub> O <sup>+</sup>	+	A <sup>-</sup>
Initial Concentration	$C_{\text{acid}}$						$C_{\text{salt}}$
Equilibrium Concentration	$C_{\text{acid}} - X$				X		$C_{\text{salt}} + X$

Equilibrium expression:

$$K_a = \frac{(C_{\text{salt}} + X) \cdot X}{C_{\text{acid}} - X}$$

Assuming X is smaller than [acid] and [salt], this reduces to:

$$K_a = \frac{(C_{\text{salt}}) \cdot (X)}{(C_{\text{acid}})}$$

Solving for X:

$$X := \frac{K_a \cdot C_{\text{acid}}}{C_{\text{salt}}}$$

$$X = 1.4721 \times 10^{-5} \text{ M}$$

Equilibrium Concentrations:

$$C_{\text{HA}} := C_{\text{acid}} - X \qquad C_{\text{HA}} = 0.124 \text{ M}$$

$$C_{\text{H}_3\text{O}} := X \qquad C_{\text{H}_3\text{O}} = 1.472 \times 10^{-5} \text{ M}$$

$$C_{\text{A}} := C_{\text{salt}} + X \qquad C_{\text{A}} = 0.152 \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) \qquad \text{pH} = 4.832$$

$$\text{pOH} := 14 - \text{pH} \qquad \text{pOH} = 9.168$$

Solving for X without assumptions (You will need to use the quadratic equation):

$$K_a = \frac{(C_{\text{salt}} + X) \cdot X}{C_{\text{acid}} - X}$$

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{\text{salt}} + \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{\text{salt}} + C_{\text{salt}}^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{\text{salt}} - \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{\text{salt}} + C_{\text{salt}}^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \end{array} \right)$$

$$X = \left( \begin{array}{l} 1.4718 \times 10^{-5} \\ -1.5165 \times 10^{-1} \end{array} \right) \text{ M}$$

Equilibrium Concentrations (Calculated for both roots, select the reasonable answer [top or bottom in {}]):

$$C_{\text{HA}} := C_{\text{acid}} - X \qquad C_{\text{HA}} = \left( \begin{array}{l} 0.124 \\ 0.276 \end{array} \right) \text{ M}$$

$$C_{\text{H}_3\text{O}} := X \qquad C_{\text{H}_3\text{O}} = \left( \begin{array}{l} 1.472 \times 10^{-5} \\ -0.152 \end{array} \right) \text{ M}$$

$$C_{\text{A}} := X \qquad C_{\text{A}} = \left( \begin{array}{l} 1.472 \times 10^{-5} \\ -0.152 \end{array} \right) \text{ M}$$

$$i := 0, 1 \dots 1$$

$$\text{pH}_i := -\log(C_{\text{H}_3\text{O}}_i \cdot \text{M}^{-1}) \qquad \text{pH} = \left( \begin{array}{l} 4.832 \\ 0.819 - 1.364i \end{array} \right)$$

$$\text{pOH} := 14 - \text{pH} \qquad \text{pOH} = \left( \begin{array}{l} 9.168 \\ 13.181 + 1.364i \end{array} \right)$$

4. Determine the pH and pOH of a buffer prepared by adding 0.0100 g of sodium hydroxide to 100 mL of 0.124 M acetic acid. Calculate using the Henderson-Hasselbalch equation (as shown in your textbook), the method of successive approximations, and using the quadratic equation (as shown in class).

Given a buffer prepared from a weak acid where (Input appropriate value here):

$$K_a := 1.8 \cdot 10^{-5} \cdot M$$

The concentration and volume of the acid is:

$$C_{\text{acid}} := 0.124 \cdot M \quad V_{\text{acid}} := 100 \cdot \text{mL}$$

Since sodium hydroxide is a strong base it will react completely with the strongest available acid (the acetic acid). This reaction will convert acetic acid into acetate.

The moles of acid present initially

$$\text{mole}_{\text{acid}} := C_{\text{acid}} \cdot V_{\text{acid}}$$

$$\text{mole}_{\text{acid}} = 0.012 \text{ mole}$$

The moles of sodium hydroxide added

$$\text{mass}_{\text{base}} := 0.0100 \cdot \text{gm}$$

$$MW_{\text{base}} := (22.990 + 15.999 + 1.0079) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{\text{base}} := \frac{\text{mass}_{\text{base}}}{MW_{\text{base}}}$$

$$\text{mole}_{\text{base}} = 2.5 \times 10^{-4} \text{ mole}$$

Since this reaction goes to completion:

$$\text{mole}_{\text{acetate}} := \text{mole}_{\text{base}} \quad \text{mole}_{\text{acetate}} = 2.5 \times 10^{-4} \text{ mole}$$

$$\text{mole}_{\text{acid}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{base}} \quad \text{mole}_{\text{acid}} = 0.012 \text{ mole}$$

$$C_{\text{acid}} := \frac{\text{mole}_{\text{acid}}}{V_{\text{acid}}}$$

$$C_{\text{acetate}} := \frac{\text{mole}_{\text{acetate}}}{V_{\text{acid}}}$$

The equilibrium solution for	HA + H <sub>2</sub> O	<->	H <sub>3</sub> O <sup>+</sup> + A <sup>-</sup>
Initial Concentration	C <sub>acid</sub>		C <sub>acetate</sub>
Equilibrium Concentration	C <sub>acid</sub> - X		X C <sub>acetate</sub> + X

Equilibrium expression:

$$K_a = \frac{(C_{\text{acetate}} + X) \cdot X}{C_{\text{acid}} - X}$$

Assuming X is smaller than [acid] and [salt], this reduces to:

$$K_a = \frac{(C_{\text{acetate}}) \cdot (X)}{(C_{\text{acid}})}$$

Solving for X:

$$X := \frac{K_a \cdot C_{\text{acid}}}{C_{\text{acetate}}}$$

$$X = 8.7473 \times 10^{-4} \text{ M}$$

Equilibrium Concentrations:

$$C_{\text{HA}} := C_{\text{acid}} - X$$

$$C_{\text{HA}} = 0.121 \text{ M}$$

$$C_{\text{H}_3\text{O}^+} := X$$

$$C_{\text{H}_3\text{O}^+} = 8.747 \times 10^{-4} \text{ M}$$

$$C_{\text{A}^-} := C_{\text{acetate}} + X$$

$$C_{\text{A}^-} = 3.375 \times 10^{-3} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1})$$

$$\text{pH} = 3.058$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 10.942$$

Solving for X without assumptions:

$$K_a = \frac{(C_{\text{salt}} + X) \cdot X}{C_{\text{acid}} - X}$$

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{\text{acetate}} + \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{\text{acetate}} + C_{\text{acetate}}^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{\text{acetate}} - \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{\text{acetate}} + C_{\text{acetate}}^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \end{array} \right)$$

$$X = \left( \begin{array}{l} 6.8315 \times 10^{-4} \\ -3.2013 \times 10^{-3} \end{array} \right) \text{ M}$$

Equilibrium Concentrations (Calculated for both roots, select the reasonable answer [top or bottom in ()]):

$$C_{\text{HA}} := C_{\text{acid}} - X$$

$$C_{\text{HA}} = \left( \begin{array}{l} 0.121 \\ 0.125 \end{array} \right) \text{ M}$$

$$C_{\text{H3O}} := X$$

$$C_{\text{H3O}} = \left( \begin{array}{l} 6.831 \times 10^{-4} \\ -3.201 \times 10^{-3} \end{array} \right) \text{ M}$$

$$C_{\text{A}} := X$$

$$C_{\text{A}} = \left( \begin{array}{l} 6.831 \times 10^{-4} \\ -3.201 \times 10^{-3} \end{array} \right) \text{ M}$$

$$i := 0, 1 \dots 1$$

$$\text{pH}_i := -\log(C_{\text{H3O}}_i \cdot \text{M}^{-1})$$

$$\text{pH} = \left( \begin{array}{l} 3.165 \\ 2.495 - 1.364i \end{array} \right)$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = \left( \begin{array}{l} 10.835 \\ 11.505 + 1.364i \end{array} \right)$$

5. Calculate the  $\text{H}_3\text{O}^{1+}$  concentration,  $\text{OH}^{1-}$  concentration, pH, pOH, acetic acid concentration, and the acetate ion concentration for the following experimental steps in a titration. Calculate using the Henderson-Hasselbalch equation (as shown in your textbook) and using the quadratic equation (as shown in class). Graph your results.

a. 1.00 mL of glacial acetic acid (pure acetic acid, density 1.0492 g/mL) is diluted with deionized water to a volume of 100.0 mL.

Starting with the following solution of acetic acid and determine the initial acid concentration:

$$K_a := 1.80 \cdot 10^{-5} \cdot \text{M}$$

$$V_{\text{acid}} := 1.00 \cdot \text{mL}$$

$$\text{density}_{\text{acid}} := 1.0492 \cdot \text{gm} \cdot \text{mL}^{-1}$$

$$\text{mass}_{\text{acid}} := V_{\text{acid}} \cdot \text{density}_{\text{acid}}$$

$$\text{MW}_{\text{acid}} := [(2 \cdot 12.001) + (4 \cdot 1.0079) + (2 \cdot 15.999)] \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{\text{acid}} := \frac{\text{mass}_{\text{acid}}}{\text{MW}_{\text{acid}}} \qquad \text{mole}_{\text{acid}} = 0.017 \text{ mole}$$

$$V_{\text{acid}} := 100.0 \cdot \text{mL}$$

$$C_{\text{acid}} := \frac{\text{mole}_{\text{acid}}}{V_{\text{acid}}} \qquad C_{\text{acid}} = 0.175 \text{ M}$$

The equilibrium solution for  $\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{X^2}{C_{\text{acid}}}$$

Solving for X:

$$X := \sqrt{K_a \cdot C_{\text{acid}}}$$

$$X = 1.7737 \times 10^{-3} \text{ M}$$

Equilibrium Concentrations:

$$C_{\text{HA}} := C_{\text{acid}} - X \qquad C_{\text{HA}} = 0.173 \text{ M}$$

$$C_{\text{H}_3\text{O}^+} := X \qquad C_{\text{H}_3\text{O}^+} = 1.774 \times 10^{-3} \text{ M}$$

$$C_{\text{A}^-} := X \qquad C_{\text{A}^-} = 1.774 \times 10^{-3} \text{ M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}^+} \cdot \text{M}^{-1}) \qquad \text{pH} = 2.751$$

$$\text{pOH} := 14 - \text{pH} \qquad \text{pOH} = 11.249$$

Solving for X without assumptions:

$$K_a = \frac{X^2}{C_{\text{acid}} - X}$$

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a + \frac{1}{2} \cdot \sqrt{K_a^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot \sqrt{K_a^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \end{array} \right)$$

$$X = \left( \begin{array}{l} 1.7647 \times 10^{-3} \\ -1.7827 \times 10^{-3} \end{array} \right) \text{ M}$$

Equilibrium Concentrations (Calculated for both roots, select the reasonable answer [top or bottom in ()]):

$$C_{\text{HA}} := C_{\text{acid}} - X$$

$$C_{\text{HA}} = \left( \begin{array}{l} 0.173 \\ 0.177 \end{array} \right) \text{ M}$$

$$C_{\text{H}_3\text{O}} := X$$

$$C_{\text{H}_3\text{O}} = \left( \begin{array}{l} 1.765 \times 10^{-3} \\ -1.783 \times 10^{-3} \end{array} \right) \text{ M}$$

$$C_{\text{A}} := X$$

$$C_{\text{A}} = \left( \begin{array}{l} 1.765 \times 10^{-3} \\ -1.783 \times 10^{-3} \end{array} \right) \text{ M}$$

$$i := 0, 1 \dots 1$$

$$\text{pH}_i := -\log(C_{\text{H}_3\text{O}_i} \cdot \text{M}^{-1})$$

$$\text{pH} = \left( \begin{array}{l} 2.753 \\ 2.749 - 1.364i \end{array} \right)$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = \left( \begin{array}{l} 11.247 \\ 11.251 + 1.364i \end{array} \right)$$

5-b.2.2468 g of NaOH is dissolved in deionized water to a volume of 500 mL.

The concentration of the base is:

$$\text{mass}_{\text{base}} := 2.2468 \cdot \text{gm}$$

$$\text{MW}_{\text{base}} := (22.990 + 15.999 + 1.0079) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{\text{base}} := \frac{\text{mass}_{\text{base}}}{\text{MW}_{\text{base}}}$$

$$\text{volume}_{\text{base}} := 500 \cdot \text{mL}$$

$$C_{\text{base}} := \frac{\text{mole}_{\text{base}}}{\text{volume}_{\text{base}}}$$

$$C_{\text{base}} = 0.1123 \text{ M}$$

The concentrations:

$$C_{\text{OH}} := C_{\text{base}}$$

$$C_{\text{OH}} = 0.112 \text{ M}$$

$$\text{pOH} := -\log(C_{\text{base}} \cdot \text{M}^{-1})$$

$$\text{pOH} = 0.949$$

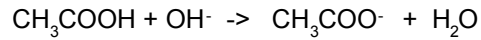
$$\text{pH} := 14 - \text{pOH}$$

$$\text{pH} = 13.051$$

5-c.0.100 mL of the sodium hydroxide solution is added to the acetic acid solution.

This shifts the equilibrium from the above system. To solve for the new equilibrium conditions, two steps are required.

First since  $\text{OH}^-$  is a strong base, and acetic acid is the strongest acid available,



This reaction will go to completion so that for:

$$\begin{aligned} C_{\text{NaOH}} &:= C_{\text{base}} & V_{\text{NaOH}} &:= 0.1 \cdot \text{mL} \\ \text{mole}_{\text{NaOH}} &:= C_{\text{NaOH}} \cdot V_{\text{NaOH}} & \text{mole}_{\text{NaOH}} &= 1.123 \times 10^{-5} \text{ mole} \\ V_{\text{total}} &:= V_{\text{acid}} + V_{\text{NaOH}} & V_{\text{total}} &= 0.1001 \text{ liter} \end{aligned}$$

The new initial, NON-EQUILIBRIUM, conditions for acetic acid and acetate are:

Acetic acid	Acetate ions
$\text{mole}_{\text{CH}_3\text{COOH}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$	$\text{mole}_{\text{CH}_3\text{COO}} := \text{mole}_{\text{NaOH}}$
$C_{\text{CH}_3\text{COOH}} := \frac{(\text{mole}_{\text{CH}_3\text{COOH}})}{V_{\text{total}}}$	$C_{\text{CH}_3\text{COO}} := \frac{(\text{mole}_{\text{CH}_3\text{COO}})}{V_{\text{total}}}$
$C_{\text{CH}_3\text{COOH}} = 1.7449 \times 10^{-1} \text{ M}$	$C_{\text{CH}_3\text{COO}} = 1.122 \times 10^{-4} \text{ M}$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{CH}_3\text{COO}} + X) \cdot X}{C_{\text{CH}_3\text{COOH}} - X}$$

Assuming X is small, we may simplify using the Henderson Hasselbach approximation

$$K_a = \frac{C_{\text{CH}_3\text{COO}} \cdot X}{C_{\text{CH}_3\text{COOH}}} \quad \text{Rearranges to:} \quad X := \frac{K_a}{C_{\text{CH}_3\text{COO}}} \cdot C_{\text{CH}_3\text{COOH}}$$

Which solves as:  $X = 0.028 \text{ M}$

This gives the following equilibrium concentrations:

$C_{\text{HA}} := C_{\text{CH}_3\text{COOH}} - X$	$C_{\text{HA}} = 0.147 \text{ M}$
$C_{\text{A}} := C_{\text{CH}_3\text{COO}} + X$	$C_{\text{A}} = 0.028 \text{ M}$
$C_{\text{H}_3\text{O}} := X$	$C_{\text{H}_3\text{O}} = 0.028 \text{ M}$
$\text{pH} := -1 \cdot \log\left(\frac{C_{\text{H}_3\text{O}}}{\text{M}}\right)$	$\text{pH} = 1.553$
$\text{pOH} := 14 - \text{pH}$	$\text{pOH} = 12.447$

If  $[H_3O^+]$  is smaller than the buffer concentrations, the answer is acceptable. In this example the approximation is not very good. Without making the Henderson Hasselbach approximation, the above problem solves as:

$$K_a = \frac{(C_{CH_3COO} + X) \cdot X}{C_{CH_3COOH} - X}$$

Has solutions (using the quadratic equation)

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} - \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} + \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \end{array} \right)$$

$$X = \left( \begin{array}{l} -1.839 \times 10^{-3} \\ 1.708 \times 10^{-3} \end{array} \right) \text{ M}$$

Selecting the appropriate root:  
(NOTE: this answer is significantly different from above.)

This gives the following equilibrium concentrations:

$$\begin{array}{ll} C_{HA} := C_{CH_3COOH} - X & C_{HA} = \left( \begin{array}{l} 0.176 \\ 0.173 \end{array} \right) \text{ M} \\ C_A := C_{CH_3COO} + X & C_A = \left( \begin{array}{l} -1.726 \times 10^{-3} \\ 1.821 \times 10^{-3} \end{array} \right) \text{ M} \\ C_{H_3O} := X & C_{H_3O} = \left( \begin{array}{l} -1.839 \times 10^{-3} \\ 1.708 \times 10^{-3} \end{array} \right) \text{ M} \\ pH_i := -1 \cdot \log \left( \frac{C_{H_3O_i}}{M} \right) & pH = \left( \begin{array}{l} 2.736 - 1.364i \\ 2.767 \end{array} \right) \\ pOH := 14 - pH & pOH = \left( \begin{array}{l} 11.264 + 1.364i \\ 11.233 \end{array} \right) \end{array}$$

5-d. 1.00 mL of the sodium hydroxide solution is added to the acetic acid solution.

$$V_{\text{NaOH}} := 1 \cdot \text{mL}$$

$$\text{mole}_{\text{NaOH}} := C_{\text{NaOH}} \cdot V_{\text{NaOH}} \quad \text{mole}_{\text{NaOH}} = 1.123 \times 10^{-4} \text{ mole}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{NaOH}} \quad V_{\text{total}} = 0.101 \text{ liter}$$

The new initial, NON-EQUILIBRIUM, conditions for acetic acid and acetate are:

Acetic acid

Acetate ions

$$\text{mole}_{\text{CH}_3\text{COOH}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$$

$$\text{mole}_{\text{CH}_3\text{COO}} := \text{mole}_{\text{NaOH}}$$

$$C_{\text{CH}_3\text{COOH}} := \frac{(\text{mole}_{\text{CH}_3\text{COOH}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COO}} := \frac{(\text{mole}_{\text{CH}_3\text{COO}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COOH}} = 1.7193 \times 10^{-1} \text{ M}$$

$$C_{\text{CH}_3\text{COO}} = 1.112 \times 10^{-3} \text{ M}$$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{CH}_3\text{COO}} + X) \cdot X}{C_{\text{CH}_3\text{COOH}} - X}$$

Assuming X is small, we may simplify using the Henderson Hasselbach approximation

$$K_a = \frac{C_{\text{CH}_3\text{COO}} \cdot X}{C_{\text{CH}_3\text{COOH}}} \quad \text{Rearranges to:} \quad X := \frac{K_a}{C_{\text{CH}_3\text{COO}}} \cdot C_{\text{CH}_3\text{COOH}}$$

Which solves as:  $X = 2.782 \times 10^{-3} \text{ M}$

This gives the following equilibrium concentrations:

$$C_{\text{HA}} := C_{\text{CH}_3\text{COOH}} - X \quad C_{\text{HA}} = 0.169 \text{ M}$$

$$C_{\text{A}} := C_{\text{CH}_3\text{COO}} + X \quad C_{\text{A}} = 3.895 \times 10^{-3} \text{ M}$$

$$C_{\text{H}_3\text{O}} := X \quad C_{\text{H}_3\text{O}} = 2.782 \times 10^{-3} \text{ M}$$

$$\text{pH} := -1 \cdot \log\left(\frac{C_{\text{H}_3\text{O}}}{\text{M}}\right) \quad \text{pH} = 2.556$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 11.444$$

If  $[H_3O^+]$  is smaller than the buffer concentrations, the answer is acceptable. In this example the approximation is not very good. Without making the Henderson Hasselbach approximation, the above problem solves as:

$$K_a = \frac{(C_{CH_3COO} + X) \cdot X}{C_{CH_3COOH} - X}$$

Has solutions (using the quadratic equation)

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} - \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} + \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \end{array} \right)$$

$$X = \left( \begin{array}{l} -2.413 \times 10^{-3} \\ 1.283 \times 10^{-3} \end{array} \right) \text{ M}$$

Selecting the appropriate root:  
(NOTE: this answer is significantly different from above.)

This gives the following equilibrium concentrations:

$$\begin{array}{ll} C_{HA} := C_{CH_3COOH} - X & C_{HA} = \left( \begin{array}{l} 0.174 \\ 0.171 \end{array} \right) \text{ M} \\ C_A := C_{CH_3COO} + X & C_A = \left( \begin{array}{l} -1.301 \times 10^{-3} \\ 2.395 \times 10^{-3} \end{array} \right) \text{ M} \\ C_{H_3O} := X & C_{H_3O} = \left( \begin{array}{l} -2.413 \times 10^{-3} \\ 1.283 \times 10^{-3} \end{array} \right) \text{ M} \\ pH_i := -1 \cdot \log \left( \frac{C_{H_3O_i}}{M} \right) & pH = \left( \begin{array}{l} 2.617 - 1.364i \\ 2.892 \end{array} \right) \\ pOH := 14 - pH & pOH = \left( \begin{array}{l} 11.383 + 1.364i \\ 11.108 \end{array} \right) \end{array}$$

5-e. 10.00 mL of the sodium hydroxide solution is added to the acetic acid solution.

$$V_{\text{NaOH}} := 10 \cdot \text{mL}$$

$$\text{mole}_{\text{NaOH}} := C_{\text{NaOH}} \cdot V_{\text{NaOH}} \quad \text{mole}_{\text{NaOH}} = 1.123 \times 10^{-3} \text{ mole}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{NaOH}} \quad V_{\text{total}} = 0.11 \text{ liter}$$

The new initial, NON-EQUILIBRIUM, conditions for acetic acid and acetate are:

Acetic acid

Acetate ions

$$\text{mole}_{\text{CH}_3\text{COOH}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$$

$$\text{mole}_{\text{CH}_3\text{COO}} := \text{mole}_{\text{NaOH}}$$

$$C_{\text{CH}_3\text{COOH}} := \frac{(\text{mole}_{\text{CH}_3\text{COOH}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COO}} := \frac{(\text{mole}_{\text{CH}_3\text{COO}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COOH}} = 1.4867 \times 10^{-1} \text{ M}$$

$$C_{\text{CH}_3\text{COO}} = 0.01 \text{ M}$$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{CH}_3\text{COO}} + X) \cdot X}{C_{\text{CH}_3\text{COOH}} - X}$$

Assuming X is small, we may simplify using the Henderson Hasselbach approximation

$$K_a = \frac{C_{\text{CH}_3\text{COO}} \cdot X}{C_{\text{CH}_3\text{COOH}}} \quad \text{Rearranges to:} \quad X := \frac{K_a}{C_{\text{CH}_3\text{COO}}} \cdot C_{\text{CH}_3\text{COOH}}$$

Which solves as:  $X = 2.62 \times 10^{-4} \text{ M}$

This gives the following equilibrium concentrations:

$$C_{\text{HA}} := C_{\text{CH}_3\text{COOH}} - X \quad C_{\text{HA}} = 0.148 \text{ M}$$

$$C_{\text{A}} := C_{\text{CH}_3\text{COO}} + X \quad C_{\text{A}} = 0.01 \text{ M}$$

$$C_{\text{H}_3\text{O}} := X \quad C_{\text{H}_3\text{O}} = 2.62 \times 10^{-4} \text{ M}$$

$$\text{pH} := -1 \cdot \log\left(\frac{C_{\text{H}_3\text{O}}}{\text{M}}\right) \quad \text{pH} = 3.582$$

$$\text{pOH} := 14 - \text{pH} \quad \text{pOH} = 10.418$$

If  $[H_3O^+]$  is smaller than the buffer concentrations, the answer is acceptable. In this example the approximation is not very good. Without making the Henderson Hasselbach approximation, the above problem solves as:

$$K_a = \frac{(C_{CH_3COO} + X) \cdot X}{C_{CH_3COOH} - X}$$

Has solutions (using the quadratic equation)

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} - \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot C_{CH_3COO} + \frac{1}{2} \cdot \sqrt{K_a^2 + 2 \cdot K_a \cdot C_{CH_3COO} + C_{CH_3COO}^2 + 4 \cdot K_a \cdot C_{CH_3COOH}} \end{array} \right)$$

$$X = \left( \begin{array}{l} -0.01 \\ 2.552 \times 10^{-4} \end{array} \right) M \quad \text{Selecting the appropriate root:} \\ \text{(NOTE: this answer is significantly different from above.)}$$

This gives the following equilibrium concentrations:

$$\begin{array}{ll} C_{HA} := C_{CH_3COOH} - X & C_{HA} = \left( \begin{array}{l} 0.159 \\ 0.148 \end{array} \right) M \\ C_A := C_{CH_3COO} + X & C_A = \left( \begin{array}{l} -2.732 \times 10^{-4} \\ 0.01 \end{array} \right) M \\ C_{H_3O} := X & C_{H_3O} = \left( \begin{array}{l} -0.01 \\ 2.552 \times 10^{-4} \end{array} \right) M \\ pH_i := -1 \cdot \log \left( \frac{C_{H_3O_i}}{M} \right) & pH = \left( \begin{array}{l} 1.979 - 1.364i \\ 3.593 \end{array} \right) \\ pOH := 14 - pH & pOH = \left( \begin{array}{l} 12.021 + 1.364i \\ 10.407 \end{array} \right) \end{array}$$

5-f. Enough sodium hydroxide solution is added to reach the equivalence point.

At the equivalence point the same number of moles of sodium hydroxide have been added as there are moles of acetic acid to begin with.

$$\text{mole}_{\text{acid}} = 0.017 \text{ mole}$$

$$\text{mole}_{\text{NaOH}} := \text{mole}_{\text{acid}}$$

$$V_{\text{NaOH}} := \frac{\text{mole}_{\text{NaOH}}}{C_{\text{base}}} \quad V_{\text{NaOH}} = 155.564 \text{ mL}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{NaOH}} \quad V_{\text{total}} = 0.25556 \text{ liter}$$

The new initial, NON-EQUILIBRIUM, conditions for acetic acid and acetate are:

Acetic acid

Acetate ions

$$\text{mole}_{\text{CH}_3\text{COOH}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$$

$$\text{mole}_{\text{CH}_3\text{COO}} := \text{mole}_{\text{NaOH}}$$

$$C_{\text{CH}_3\text{COOH}} := \frac{(\text{mole}_{\text{CH}_3\text{COOH}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COO}} := \frac{(\text{mole}_{\text{CH}_3\text{COO}})}{V_{\text{total}}}$$

$$C_{\text{CH}_3\text{COOH}} = 0 \text{ M}$$

$$C_{\text{CH}_3\text{COO}} = 0.068 \text{ M}$$

$$K_b := \frac{K_w}{K_a} \quad K_b = 5.556 \times 10^{-10} \text{ M}$$

The equilibrium solution for

A-	+	H <sub>2</sub> O	<->	OH-	+	HA
Initial Concentration						

Equilibrium Concentration						

Equilibrium expression:

$$K_b = \frac{X^2}{C_{\text{CH}_3\text{COO}} - X}$$

Assuming X is smaller than [acid], this reduces to:

$$K_b = \frac{X^2}{C_{\text{CH}_3\text{COO}}}$$

Solving for X:

$$X := \sqrt{K_b \cdot C_{\text{CH}_3\text{COO}}} \quad X = 6.1639 \times 10^{-6} \text{ M}$$

Equilibrium Concentrations:

$$C_{\text{HA}} := X \quad C_{\text{HA}} = 6.164 \times 10^{-6} \text{ M}$$

$$C_{\text{OH}} := X \quad C_{\text{OH}} = 6.164 \times 10^{-6} \text{ M}$$

$$C_{\text{A}} := C_{\text{CH}_3\text{COO}} - X \quad C_{\text{A}} = 0.068 \text{ M}$$

$$\text{pOH} := -\log(C_{\text{OH}} \cdot \text{M}^{-1}) \quad \text{pOH} = 5.21$$

$$\text{pH} := 14 - \text{pOH} \quad \text{pH} = 8.79$$

Solving for X without assumptions:

$$K_b = \frac{X^2}{C_{\text{CH}_3\text{COO}} - X}$$

$$X := \left( \begin{array}{l} \frac{-1}{2} \cdot K_b + \frac{1}{2} \cdot \sqrt{K_b^2 + 4 \cdot K_b \cdot C_{\text{CH}_3\text{COO}}} \\ \frac{-1}{2} \cdot K_b - \frac{1}{2} \cdot \sqrt{K_b^2 + 4 \cdot K_b \cdot C_{\text{CH}_3\text{COO}}} \end{array} \right) \quad X = \left( \begin{array}{l} 6.1636 \times 10^{-6} \\ -6.1641 \times 10^{-6} \end{array} \right) \text{ M}$$

Equilibrium Concentrations (Calculated for both roots, select the reasonable answer [top or bottom in ( )]):

$$C_{\text{HA}} := X \quad C_{\text{HA}} = \left( \begin{array}{l} 6.164 \times 10^{-6} \\ -6.164 \times 10^{-6} \end{array} \right) \text{ M}$$

$$C_{\text{OH}} := X \quad C_{\text{OH}} = \left( \begin{array}{l} -0.01 \\ 2.552 \times 10^{-4} \end{array} \right) \text{ M}$$

$$C_{\text{A}} := C_{\text{CH}_3\text{COO}} - X \quad C_{\text{A}} = \left( \begin{array}{l} 0.068 \\ 0.068 \end{array} \right) \text{ M}$$

$$\text{pOH}_1 := -\log(C_{\text{OH}_1} \cdot \text{M}^{-1}) \quad \text{pOH} = \left( \begin{array}{l} 5.21 \\ 5.21 - 1.364i \end{array} \right)$$

$$\text{pH} := 14 - \text{pOH} \quad \text{pH} = \left( \begin{array}{l} 8.79 \\ 8.79 + 1.364i \end{array} \right)$$

5-g. 160.00 mL of the sodium hydroxide solution is added to the acetic acid solution.

This is an excess of NaOH. Since  $\text{OH}^-$  is the strongest base present it will determine the pH

$$V_{\text{NaOH}} := 160 \cdot \text{mL}$$

$$\text{mole}_{\text{NaOH}} := C_{\text{NaOH}} \cdot V_{\text{NaOH}}$$

$$\text{mole}_{\text{NaOH}} = 0.018 \text{ mole}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{NaOH}}$$

$$V_{\text{total}} = 0.26 \text{ liter}$$

First  $\text{OH}^-$  will convert all the  $\text{CH}_3\text{COOH}$  to  $\text{CH}_3\text{COO}^-$  these initial conditions are:

$$\text{mole}_{\text{CH}_3\text{COOH}} := 0$$

$$\text{mole}_{\text{CH}_3\text{COO}^-} := \text{mole}_{\text{acid}}$$

Calculate the  $[\text{OH}^-]$ , from the excess  $\text{OH}^-$ .

$$\text{mole}_{\text{OH}^-} := \text{mole}_{\text{NaOH}} - \text{mole}_{\text{acid}}$$

$$\text{mole}_{\text{OH}^-} = 4.983 \times 10^{-4} \text{ mole}$$

$$C_{\text{OH}^-} := \frac{\text{mole}_{\text{OH}^-}}{V_{\text{total}}}$$

$$C_{\text{OH}^-} = 1.917 \times 10^{-3} \text{ M}$$

Then use this to calculate pOH and pH:

$$\text{pOH} := -\log\left(\frac{C_{\text{OH}^-}}{\text{M}}\right) \quad \text{pOH} = 2.717$$

$$\text{pH} := 14 - \text{pOH} \quad \text{pH} = 11.283$$

5-h. 200.0 mL of the sodium hydroxide solution is added to the acetic acid solution.

This is an excess of NaOH. Since  $\text{OH}^-$  is the strongest base present it will determine the pH

$$V_{\text{NaOH}} := 200 \cdot \text{mL}$$

$$\text{mole}_{\text{NaOH}} := C_{\text{NaOH}} \cdot V_{\text{NaOH}}$$

$$\text{mole}_{\text{NaOH}} = 0.022 \text{ mole}$$

$$V_{\text{total}} := V_{\text{acid}} + V_{\text{NaOH}}$$

$$V_{\text{total}} = 0.3 \text{ liter}$$

First  $\text{OH}^-$  will convert all the  $\text{CH}_3\text{COOH}$  to  $\text{CH}_3\text{COO}^-$  these initial conditions are:

$$\text{mole}_{\text{CH}_3\text{COOH}} := 0$$

$$\text{mole}_{\text{CH}_3\text{COO}^-} := \text{mole}_{\text{acid}}$$

Calculate the  $[\text{OH}^-]$ , from the excess  $\text{OH}^-$ .

$$\text{mole}_{\text{OH}^-} := \text{mole}_{\text{NaOH}} - \text{mole}_{\text{acid}}$$

$$\text{mole}_{\text{OH}^-} = 4.992 \times 10^{-3} \text{ mole}$$

$$C_{\text{OH}^-} := \frac{\text{mole}_{\text{OH}^-}}{V_{\text{total}}}$$

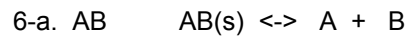
$$C_{\text{OH}^-} = 0.017 \text{ M}$$

Then use this to calculate pOH and pH:

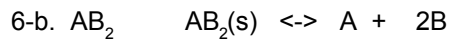
$$\text{pOH} := -\log\left(\frac{C_{\text{OH}^-}}{\text{M}}\right) \quad \text{pOH} = 1.779$$

$$\text{pH} := 14 - \text{pOH} \quad \text{pH} = 12.221$$

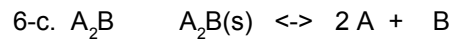
6. Assuming the molar solubility of a salt is x, write the balanced chemical equation for dissolving the solid salt, the  $K_{sp}$  expression and the  $K_{sp}$  expression solved for x.



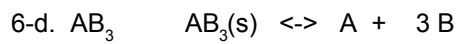
$$K_{sp} = (X) \cdot (X) \quad X = \sqrt{K_{sp}}$$



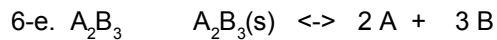
$$K_{sp} = (X) \cdot (2 \cdot X)^2$$
$$K_{sp} = 4 \cdot X^3 \quad X = \left( \frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$



$$K_{sp} = (2 \cdot X)^2 \cdot (X)$$
$$K_{sp} = 4 \cdot X^3 \quad X = \left( \frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$



$$K_{sp} = (X) \cdot (3 \cdot X)^3$$
$$K_{sp} = 27 \cdot X^4 \quad X = \left( \frac{K_{sp}}{27} \right)^{\frac{1}{4}}$$



$$K_{sp} = (2 \cdot X)^2 \cdot (3 \cdot X)^3$$
$$K_{sp} = 108 \cdot X^5 \quad X = \left( \frac{K_{sp}}{108} \right)^{\frac{1}{5}}$$

7.  $3.2 \times 10^{-3}$  g of manganese (II) hydroxide will dissolve in 1 liter of water at 25 °C. What is the pH of a saturated manganese (II) hydroxide solution? What is  $K_{sp}$  for manganese(II) hydroxide?

7-a. The pH of the solution:

First calculate the moles of  $Mn(OH)_2$  dissolved

$$\text{mass} := 3.2 \cdot 10^{-3} \cdot \text{gm}$$

$$\text{MW} := [54.938 + 2 \cdot (15.999 + 1.0079)] \cdot \frac{\text{gm}}{\text{mole}} \quad \text{MW} = 88.952 \text{ gm} \cdot \text{mole}^{-1}$$

$$\text{mole}_{MnOH2} := \frac{\text{mass}}{\text{MW}}$$

$$\text{mole}_{MnOH2} = 3.597 \times 10^{-5} \text{ mole}$$

Next calculate the concentration of  $OH^-$

$$\text{volume} := 1 \cdot \text{liter}$$

$$M := \frac{\text{mole}}{\text{liter}}$$

$$C_{OH} := \frac{2 \cdot \text{mole}_{MnOH2}}{\text{volume}}$$

$$C_{OH} = 7.195 \times 10^{-5} \text{ M}$$

Then the concentration of  $H_3O^+$

$$K_w := 1.0 \cdot 10^{-14} \cdot \text{M}^2$$

$$C_{H3O} := \frac{K_w}{C_{OH}}$$

$$C_{H3O} = 1.39 \times 10^{-10} \text{ M}$$

Then the pH

$$\text{pH} := -\log(C_{H3O} \cdot \text{M}^{-1})$$

$$\text{pH} = 9.857$$

7-b. Calculate  $K_{sp}$  for  $Mn(OH)_2$

$$C_{Mn} := \frac{C_{OH}}{2}$$

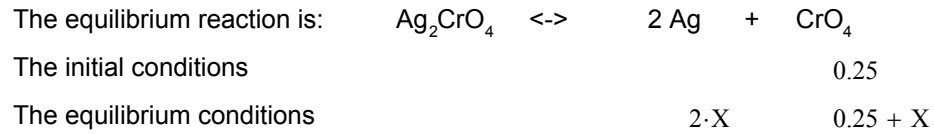
$$C_{Mn} = 3.597 \times 10^{-5} \text{ M}$$

And the appropriate expression for  $K_{sp}$

$$K_{sp} := (C_{Mn}) \cdot (C_{OH})^2$$

$$K_{sp} = 1.862 \times 10^{-13} \text{ M}^3$$

8. How many grams of silver chromate can dissolve in 250 mL of 0.25 M sodium chromate?



The equilibrium expression:

$$K_{sp} = (2 \cdot X)^2 \cdot (0.25 + X)$$

For  $\text{Ag}_2\text{CrO}_4$

$$K_{sp} := 1.1 \cdot 10^{-12}$$

If we assume that X is much smaller than 0.25, the equilibrium expression simplifies to

$$K_{sp} = (2 \cdot X)^2 \cdot (0.25)$$

simplifies to

$$K_{sp} = X^2$$

$$X := \sqrt{K_{sp}}$$

$$X = 1.049 \times 10^{-6}$$

For 250 mL of solution:

$$\text{mole}_{\text{Ag}_2\text{CrO}_4} := (X \cdot M) \cdot (0.250 \cdot \text{liter}) \quad \text{mole}_{\text{Ag}_2\text{CrO}_4} = 2.622 \times 10^{-7} \text{ mole}$$

Find the mass of silver chromate.

$$\text{MW}_{\text{Ag}_2\text{CrO}_4} := [(2 \cdot 107.8682) + 51.9961 + (4 \cdot 15.9994)] \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{MW}_{\text{Ag}_2\text{CrO}_4} = 331.73 \text{ gm} \cdot \text{mole}^{-1}$$

$$\text{Mass}_{\text{Ag}_2\text{CrO}_4} := \text{MW}_{\text{Ag}_2\text{CrO}_4} \cdot \text{mole}_{\text{Ag}_2\text{CrO}_4}$$

$$\text{Mass}_{\text{Ag}_2\text{CrO}_4} = 8.698 \times 10^{-5} \text{ gm}$$

9. 0.500 grams of lead nitrate is dissolved in 250.0 mL of water. When 10 mL of 1.0 M NaCl is added to this solution: What is the mass of the precipitate? What is the equilibrium concentration of all the ions in the solution?

Find the moles of lead nitrate dissolved:

$$\text{Mass}_{\text{PbNO}_3} := 0.500 \cdot \text{gm}$$

$$\text{MW}_{\text{PbNO}_3} := [207.2 + (2 \cdot 14.00674) + (6 \cdot 15.9994)] \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{Mole}_{\text{PbNO}_3} := \frac{\text{Mass}_{\text{PbNO}_3}}{\text{MW}_{\text{PbNO}_3}}$$

$$\text{Mole}_{\text{PbNO}_3} = 1.51 \times 10^{-3} \text{ mole}$$

Find the moles of sodium chloride added:

$$C_{\text{NaCl}} := 1.0 \cdot \text{M}$$

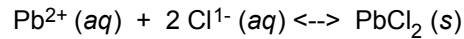
$$V_{\text{NaCl}} := 10 \cdot \text{mL}$$

$$V_{\text{NaCl}} = 0.01 \text{ liter}$$

$$\text{Mole}_{\text{NaCl}} := C_{\text{NaCl}} \cdot V_{\text{NaCl}}$$

$$\text{Mole}_{\text{NaCl}} = 0.01 \text{ mole}$$

The precipitation reaction is:



$$K_{\text{sp}} = C_{\text{Pb}} \cdot C_{\text{Cl}}^2$$

$$V := (250 + 10) \cdot \text{mL}$$

$$V = 0.26 \text{ liter}$$

$$C_{\text{Pb}} := \frac{\text{Mole}_{\text{PbNO}_3}}{V}$$

$$C_{\text{Pb}} = 5.806 \times 10^{-3} \text{ M}$$

$$C_{\text{Cl}} := \frac{\text{Mole}_{\text{NaCl}}}{V}$$

$$C_{\text{Cl}} = 0.038 \text{ M}$$

$$Q := C_{\text{Pb}} \cdot C_{\text{Cl}}^2$$

$$Q = 8.589 \times 10^{-6} \text{ M}^3$$

$$K_{\text{sp}} := 1.7 \cdot 10^{-5} \cdot \text{M}^3$$

Since Q is less than  $K_{\text{sp}}$ , no precipitate is produced in this reaction.

Find the moles of lead nitrate dissolved:

$$\text{Mass}_{\text{PbNO}_3} := 0.500 \cdot \text{gm}$$

$$\text{MW}_{\text{PbNO}_3} := [207.2 + (2 \cdot 14.00674) + (6 \cdot 15.9994)] \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{Mole}_{\text{PbNO}_3} := \frac{\text{Mass}_{\text{PbNO}_3}}{\text{MW}_{\text{PbNO}_3}}$$

$$\text{Mole}_{\text{PbNO}_3} = 1.51 \times 10^{-3} \text{ mole}$$

Find the moles of sodium chloride added:

$$C_{\text{NaCl}} := 2.0 \cdot \text{M}$$

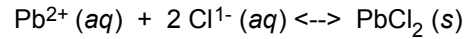
$$V_{\text{NaCl}} := 20 \cdot \text{mL}$$

$$V_{\text{NaCl}} = 0.02 \text{ liter}$$

$$\text{Mole}_{\text{NaCl}} := C_{\text{NaCl}} \cdot V_{\text{NaCl}}$$

$$\text{Mole}_{\text{NaCl}} = 0.04 \text{ mole}$$

The precipitation reaction is:



$$K_{\text{sp}} = C_{\text{Pb}} \cdot C_{\text{Cl}}^2$$

$$V := (250 + 20) \cdot \text{mL}$$

$$V = 0.27 \text{ liter}$$

$$C_{\text{Pb}} := \frac{\text{Mole}_{\text{PbNO}_3}}{V}$$

$$C_{\text{Pb}} = 5.591 \times 10^{-3} \text{ M}$$

$$C_{\text{Cl}} := \frac{\text{Mole}_{\text{NaCl}}}{V}$$

$$C_{\text{Cl}} = 0.148 \text{ M}$$

$$Q := C_{\text{Pb}} \cdot C_{\text{Cl}}^2$$

$$Q = 1.227 \times 10^{-4} \text{ M}^3$$

$$K_{\text{sp}} := 1.7 \cdot 10^{-5} \cdot \text{M}^3$$

Q is greater than  $K_{\text{sp}}$  so a precipitate is produced



Back to the equilibrium expression:

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (0.14815 - X)^2$$

The problem is greatly simplified if we "assume" that X is much smaller than 0.14815.

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (0.14815)^2$$

$$1.7 \cdot 10^{-5} = 1.22691681775 \cdot 10^{-4} - 2.19484225 \cdot 10^{-2} \cdot X$$

$$X = 4.8154 \cdot 10^{-3}$$

We can check the assumption by evaluating the original expression with this value of X

$$1.7 \cdot 10^{-5} = (0.00559 - 4.8154 \cdot 10^{-3}) \cdot (0.14815 - 4.8154 \cdot 10^{-3})^2$$

$$1.7 \cdot 10^{-5} = 1.591 \cdot 10^{-5}$$

This is fairly close, so the approximation was pretty good. We can now improve the calculated value of X by using this value for a successive approximation and substitute it into part of the original expression (instead of the assuming that X is much smaller than 0.14815 to simplify the calculation, we use this value). So Back to the original expression:

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (0.14815 - X)^2$$

Make the substitution:

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (0.14815 - 4.8154 \cdot 10^{-3})^2$$

And solve for the remaining X:

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (.1433346)^2$$

$$1.7 \cdot 10^{-5} = (0.00559 - X) \cdot (2.054480755716 \cdot 10^{-2})$$

$$1.7 \cdot 10^{-5} = 1.148454742445244 \cdot 10^{-4} - 2.054480755716 \cdot 10^{-2} \cdot X$$

$$X = 4.762 \cdot 10^{-3}$$

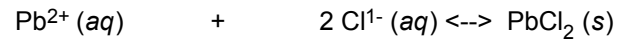
This value of X should be a bit better than the first estimate, so we go back and substitute it into the original expression and see how it works:

$$1.7 \cdot 10^{-5} = (0.00559 - 4.762 \cdot 10^{-3}) \cdot (0.14815 - 4.762 \cdot 10^{-3})^2$$

$$1.7 \cdot 10^{-5} = 1.7023778154432 \cdot 10^{-5}$$

Which is a very good agreement. It also compares well with the value calculated by solving the cubic expression.

So now we can determine the equilibrium concentrations of all the species and the mass of the precipitate. Remember that:



Initial Conditions:  $C_{\text{Pb}} = 5.591 \times 10^{-3} \text{ M}$        $C_{\text{Cl}} = 0.148 \text{ M}$

Change:  $-X$        $-2 \cdot X$

From above we found the solution for X

$$X := 4.762 \cdot 10^{-3} \cdot \text{M}$$

So the equilibrium concentrations are:

$$C_{\text{Pb\_equilibrium}} := C_{\text{Pb}} - X \qquad C_{\text{Pb\_equilibrium}} = 8.292 \times 10^{-4} \text{ M}$$

$$C_{\text{Cl\_equilibrium}} := C_{\text{Cl}} - 2 \cdot X \qquad C_{\text{Cl\_equilibrium}} = 0.139 \text{ M}$$

The amount of precipitate is:

$$\text{Mole}_{\text{PbCl}_2} := X \cdot V$$

$$\text{Mole}_{\text{PbCl}_2} = 1.286 \times 10^{-3} \text{ mole}$$

$$\text{MW}_{\text{PbCl}_2} := (207.2 + 2 \cdot 35.4527) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{Mass}_{\text{PbCl}_2} := \text{Mole}_{\text{PbCl}_2} \cdot \text{MW}_{\text{PbCl}_2}$$

$$\text{Mass}_{\text{PbCl}_2} = 0.358 \text{ gm}$$