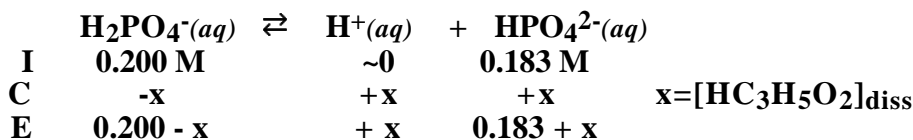


ALL work must be shown in all problems for full credit. **Due at the beginning of class on Wednesday, December 5, 2001.**

PS14.1. Phosphate buffers are commonly used in soft drinks to help control the pH. What is the pH of a soft drink in which the major buffer components are 8.50 g of NaH_2PO_4 and 9.23 g of Na_2HPO_4 per 355 mLs of solution?

$$8.50 \text{ g NaH}_2\text{PO}_4 \left(\frac{1 \text{ mol}}{120 \text{ g}} \right) \left(\frac{1}{0.355 \text{ L}} \right) = 0.200 \text{ M}$$

$$9.23 \text{ g Na}_2\text{HPO}_4 \left(\frac{1 \text{ mol}}{142 \text{ g}} \right) \left(\frac{1}{0.355 \text{ L}} \right) = 0.183 \text{ M}$$



$$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]}$$

$$6.2 \times 10^{-8} = \frac{(x)(0.183x)}{(0.200 - x)} \quad x \lll 0.183$$

$$6.2 \times 10^{-8} = \frac{(x)0.183}{0.200}$$

$$6.78 \times 10^{-8} \text{ M} = x = [\text{H}^+]$$

$$\text{pH} = 7.17$$

PS14.2. Specify the reagents (an acid and its conjugate base or a base and its conjugate acid) and the concentration of each reagent needed to prepare buffer solutions having the listed pH values.

NOTE: The optimum buffer solution is one with equal concentrations of the weak acid (weak base) and its conjugate base (conjugate acid). Under these conditions, the pH of the solution is equal to the $\text{p}K_a$ ($\text{p}K_b$). So the best reagent for each of the solutions below is one whose $\text{p}K$ is equal to the pH. Since the tables in the appendix list K values, each of the pH's must be converted to their corresponding $[\text{H}^+]$ and compared to an equilibrium constant in Appendix D.

a) 4.74

pH = 4.74 : $[\text{H}^+] = 1.8 \times 10^{-5}$ Acetic acid has a $K_a = 1.8 \times 10^{-5}$; therefore, a solution of .85 M $\text{HC}_2\text{H}_3\text{O}_2$ and .85 M $\text{NaC}_2\text{H}_3\text{O}_2$ would have a pH of 4.74.

b) 9.81

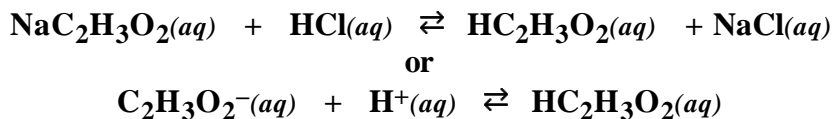
pH = 9.81 : $[\text{H}^+] = 1.54 \times 10^{-10}$ M and $[\text{OH}^-] = 6.4 \times 10^{-5}$ M. Since the pH is basic, a weak base and its conjugate acid should be considered. Ethylamine has a $K_b = 6.4 \times 10^{-5}$; therefore, a solution of 0.70 M $(\text{CH}_3)_2\text{N}$ and . M $(\text{CH}_3)_2\text{NHCl}$ would have a pH of 9.81.

c) 2.92

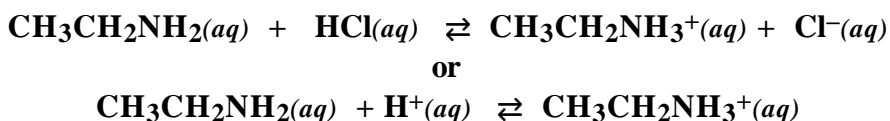
pH = 2.92 : $[\text{H}^+] = 1.2 \times 10^{-3}$ Chloroacetic acid has a $K_a = 1.4 \times 10^{-3}$; therefore, a solution of .65 M $\text{HC}_2\text{H}_2\text{O}_2\text{Cl}$ and .76 M $\text{NaC}_2\text{H}_2\text{O}_2\text{Cl}$ would have a pH of 4.74.

PS14.3. Write the reaction that occurs when a strong acid is added to each of the buffer solutions below.

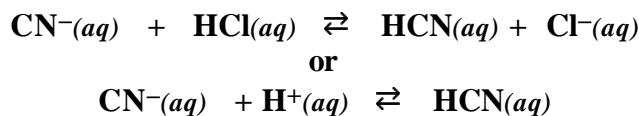
a) $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$



d) $\text{C}_2\text{H}_5\text{NH}_3/\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$

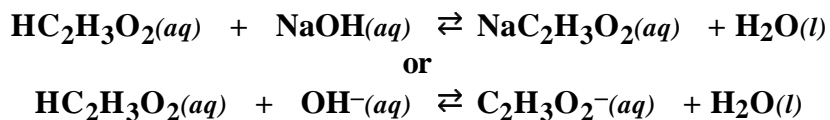


c) HCN/KCN

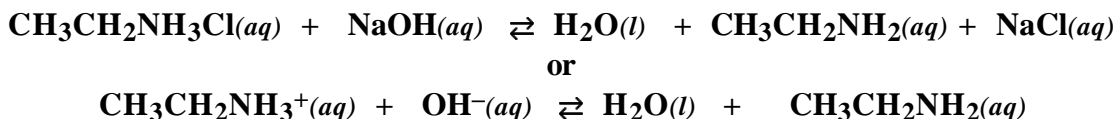


PS14.4. Write the reaction that occurs when a strong base is added to each of the buffer solutions below.

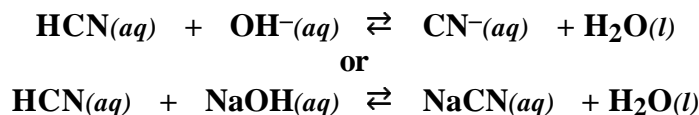
a) $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$



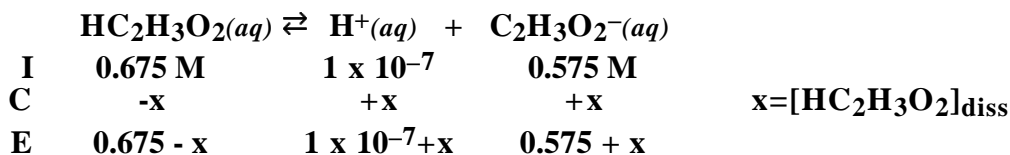
b) $\text{C}_2\text{H}_5\text{NH}_3/\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$



c) HCN/KCN



PS14.5. Determine the pH of a buffer prepared by mixing 0.675 moles of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.575 moles of $\text{NaC}_2\text{H}_3\text{O}_2$ in enough water to give 1.00 liter of solution.



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

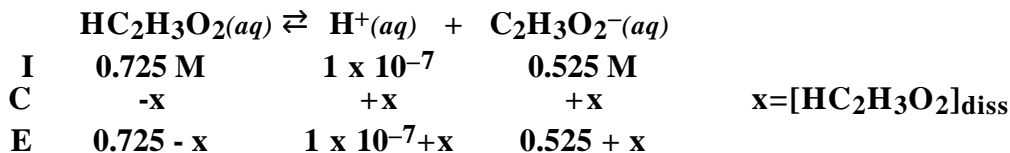
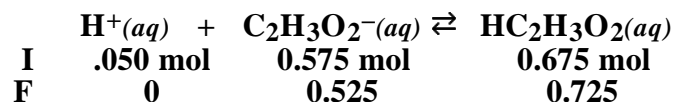
$$1.8 \times 10^{-5} = \frac{(0.575 + x)(1 \times 10^{-7} + x)}{(0.675 - x)} \quad x < 0.475 \text{ and } x > 1 \times 10^{-7}$$

$$1.8 \times 10^{-5} = \frac{0.575(x)}{0.675}$$

$$2.1 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.68$$

Calculate the pH when

a) 0.0500 mol of HCl is added



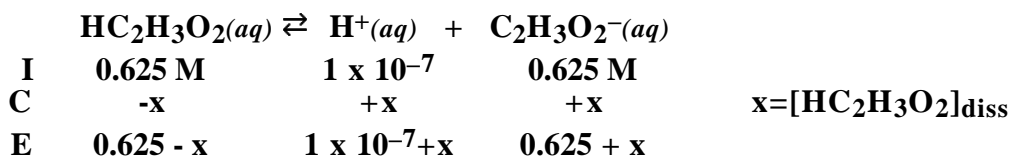
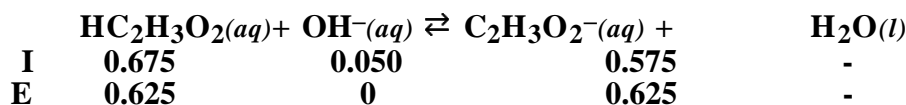
$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$1.8 \times 10^{-5} = \frac{(0.525 + x)(1 \times 10^{-7} + x)}{(0.725 - x)} \quad x < 0.475 \text{ and } x > 1 \times 10^{-7}$$

$$1.8 \times 10^{-5} = \frac{0.525(x)}{0.725}$$

$$2.5 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.60$$

b) 0.0500 mol of NaOH is added



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

$$1.8 \times 10^{-5} = \frac{(0.625 + x)(1 \times 10^{-7} + x)}{(0.625 - x)} \quad x < 0.625$$

$$1.8 \times 10^{-5} = \frac{0.625(x)}{0.625}$$

$$1.8 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.74$$

PS14.5. (CONTINUED)

c) 1 liter of water is added

$$M_1V_1 = M_2V_2$$

$$0.675 \text{ M} \cdot 1 \text{ L} = M_2 \cdot 2 \text{ L}$$

$$M_2 = \frac{0.675 \text{ M} \cdot 1 \text{ L}}{2 \text{ L}} = 0.338 \text{ M HC}_2\text{H}_3\text{O}_2$$

$$M_1V_1 = M_2V_2$$

$$0.575 \text{ M} \cdot 1 \text{ L} = M_2 \cdot 2 \text{ L}$$

$$M_2 = \frac{0.575 \text{ M} \cdot 1 \text{ L}}{2 \text{ L}} = 0.288 \text{ M C}_2\text{H}_3\text{O}_2^-$$



	I	0.338 M	1×10^{-7}	0.288 M
--	---	---------	--------------------	---------

	C	-x	+x	+x
--	---	----	----	----

	E	$0.338 - x$	$1 \times 10^{-7} + x$	$0.288 + x$
--	---	-------------	------------------------	-------------

$$x = [\text{HC}_2\text{H}_3\text{O}_2]_{\text{diss}}$$

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

$$1.8 \times 10^{-5} = \frac{(0.288 + x)(1 \times 10^{-7} + x)}{(0.338 - x)} \quad x < 0.288 \text{ M}$$

$$1.8 \times 10^{-5} = \frac{0.288(x)}{0.338}$$

$$2.1 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.68$$

Dilution has no effect on the pH of the buffer. pH = 4.79

d) 5.00 mL of a 1.00 M HNO₃ solution is added

$$\left(1.00 \frac{\text{mol}}{\text{L}}\right) 0.005 \text{ L} = 0.005 \text{ mol H}^+$$

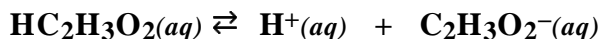


	I	0.0050 mol	0.575 mol	0.675 mol
--	---	------------	-----------	-----------

	F	0	0.570	0.680
--	---	---	-------	-------

$$\frac{0.570 \text{ mol}}{1.005 \text{ L}} = 0.567 \text{ M}$$

$$\frac{0.680 \text{ mol}}{1.005 \text{ L}} = 0.677$$



	I	0.677 M	1×10^{-7}	0.567 M
--	---	---------	--------------------	---------

	C	-x	+x	+x
--	---	----	----	----

	E	$0.677 - x$	$1 \times 10^{-7} + x$	$0.567 + x$
--	---	-------------	------------------------	-------------

$$x = [\text{HC}_2\text{H}_3\text{O}_2]_{\text{diss}}$$

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

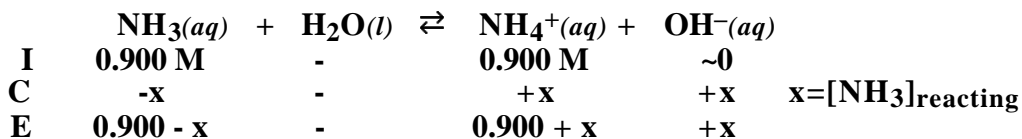
$$1.8 \times 10^{-5} = \frac{(0.567 + x)(1 \times 10^{-7} + x)}{(0.677 - x)} \quad x < 0.570$$

$$1.8 \times 10^{-5} = \frac{0.567(x)}{0.677}$$

$$2.15 \times 10^{-5} \text{ M} = x = [\text{H}^+] \quad \text{pH} = 4.67$$

PS14.6. Calculate the pH **change** produced when 0.100 mol of gaseous HCl is added to each of the following buffer solutions.

a) 500 mL of 0.900 M NH₃ and 0.900 M NH₄Cl



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

$$1.8 \times 10^{-5} = \frac{(0.900 + x)(+x)}{0.900 - x} \quad x < 0.90$$

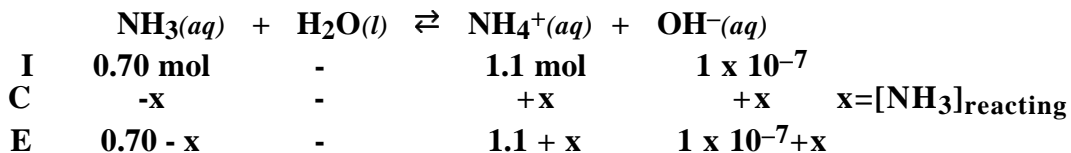
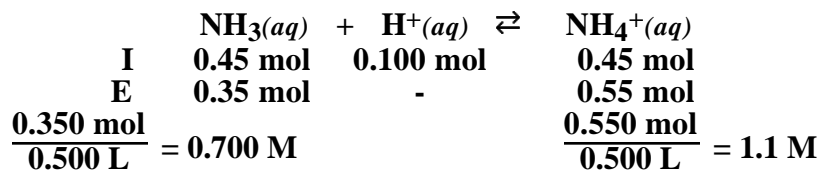
$$1.8 \times 10^{-5} = \frac{(0.90)(x)}{0.90}$$

$$1.8 \times 10^{-5} = x = [\text{OH}^-]$$

$$\text{pOH} = 4.74 \quad \text{pH} = 9.26$$

$$0.900 \frac{\text{mol}}{\text{L}} \cdot 0.500 \text{ L} = 0.450 \text{ mol NH}_3$$

$$0.900 \frac{\text{mol}}{\text{L}} \cdot 0.500 \text{ L} = 0.450 \text{ mol NH}_4^+$$



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

$$1.8 \times 10^{-5} = \frac{(1.1 + x)(1 \times 10^{-7} + x)}{0.70 - x} \quad x < 0.35 \text{ and } x > 1 \times 10^{-7}$$

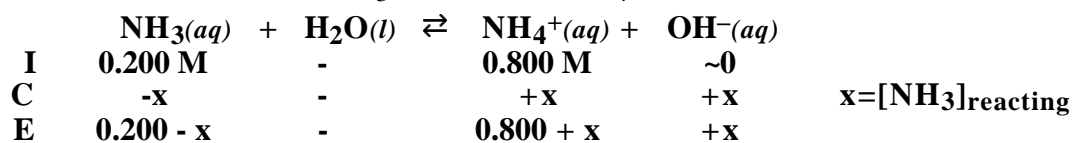
$$1.8 \times 10^{-5} = \frac{(1.1)(x)}{0.70}$$

$$1.14 \times 10^{-5} = x = [\text{OH}^-]$$

$$\text{pOH} = 4.94 \quad \text{pH} = 9.06$$

The pH change is 0.20 pH units.

b) 500 mL of 0.200 M NH₃ and 0.800 M NH₄Cl



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

$$1.8 \times 10^{-5} = \frac{(0.800 + x)(1 \times 10^{-7} + x)}{0.200 - x} \quad x < 0.20$$

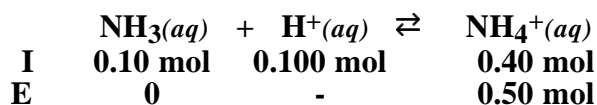
$$1.8 \times 10^{-5} = \frac{(0.80)(x)}{0.20}$$

$$4.5 \times 10^{-6} = x = [\text{OH}^-]$$

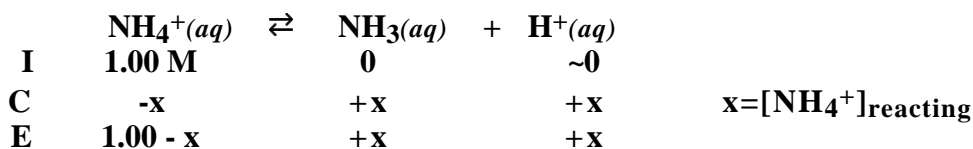
$$\text{pOH} = 5.35 \quad \text{pH} = 8.65$$

$$0.200 \frac{\text{mol}}{\text{L}} \cdot 0.500 \text{ L} = 0.100 \text{ mol NH}_3$$

$$0.800 \frac{\text{mol}}{\text{L}} \cdot 0.500 \text{ L} = 0.400 \text{ mol NH}_4^+$$



$$\frac{0.50 \text{ mol NH}_4^+}{0.500 \text{ L}} = 1.00 \text{ M}$$



$$K_a = \frac{K_w}{K_b} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{(x)(x)}{1.00 - x} \quad x < 1.00$$

$$5.56 \times 10^{-10} = \frac{(x)(x)}{1.00}$$

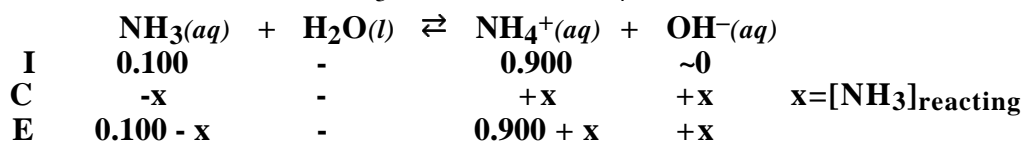
$$5.56 \times 10^{-10} = x^2$$

$$2.36 \times 10^{-5} = x = [\text{H}^+]$$

$$\text{pH} = 4.63$$

The pH change is 4.02 pH units.

c) 500 mL of 0.100 M NH₃ and 0.900 M NH₄Cl



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

$$1.8 \times 10^{-5} = \frac{(0.900 + x)(1 \times 10^{-7} + x)}{0.100 - x} \quad x < 0.10 \text{ and } x \gg 1 \times 10^{-7}$$

$$1.8 \times 10^{-5} = \frac{(0.90)(x)}{0.10}$$

$$2.0 \times 10^{-6} = x = [\text{OH}^-]$$

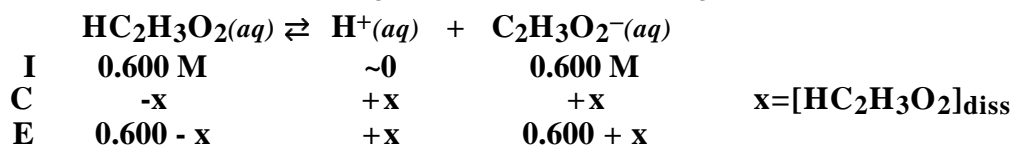
$$\text{pOH} = 5.70 \quad \text{pH} = 8.30$$

After the neutralization reaction, the solution contains 0.100 M HCl and 1.0 M NH₄⁺. The pH of a solution of a strong acid, at a high concentration, and a weak acid is dominated by the strong acid. Therefore, the pH of the solution is;

$$\text{pH} = -\log(0.100 \text{ M}) = 1.00 \quad \text{pH change is 7.30 pH units.}$$

PS14.7. Calculate the pH change produced when 0.100 mol of solid NaOH is added to each of the following buffer solutions.

a) 500 mL of 0.600 M HC₂H₃O₂ and 0.600 M NaC₂H₃O₂



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

$$1.8 \times 10^{-5} = \frac{(0.600 + x)(x)}{(0.600 - x)} \quad x < 0.600$$

$$1.8 \times 10^{-5} = \frac{0.600(x)}{0.600}$$

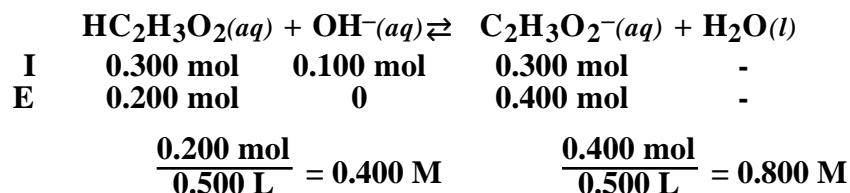
$$1.8 \times 10^{-5} \text{ M} = x = [\text{H}^+]$$

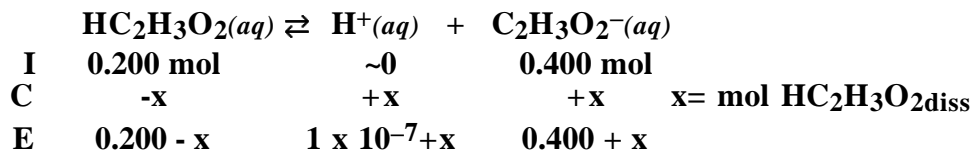
$$\text{pH} = 4.74$$

When the NaOH is added to the solution we must convert to moles of the weak acid and conjugate base.

$$0.600 \frac{\text{mol HC}_2\text{H}_3\text{O}_2}{\text{L}} \cdot 0.500 \text{ L} = 0.300 \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$0.600 \frac{\text{mol HC}_2\text{H}_3\text{O}_2}{\text{L}} \cdot 0.500 \text{ L} = 0.300 \text{ mol C}_2\text{H}_3\text{O}_2^-$$





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

$$1.8 \times 10^{-5} = \frac{(0.400 + x)(1 \times 10^{-7} + x)}{(0.200 - x)} \quad x < 0.350$$

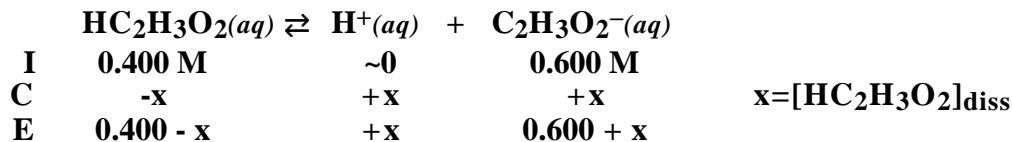
$$1.8 \times 10^{-5} = \frac{0.400(x)}{0.200}$$

$$9.0 \times 10^{-6} \text{ M} = x = [\text{H}^+]$$

$$\text{pH} = 5.04$$

The change is 0.300 pH units

b) 500 mL of 0.400 M HC₂H₃O₂ and 0.600 M NaC₂H₃O₂



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

$$1.8 \times 10^{-5} = \frac{(0.600 + x)(x)}{(0.400 - x)} \quad x < 0.600$$

$$1.8 \times 10^{-5} = \frac{0.600(x)}{0.400}$$

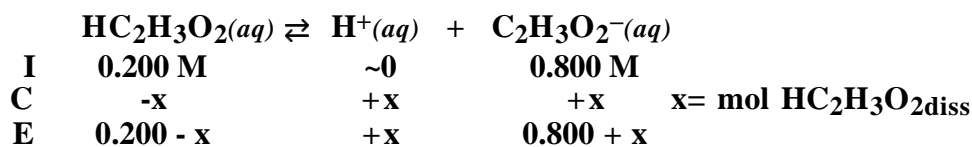
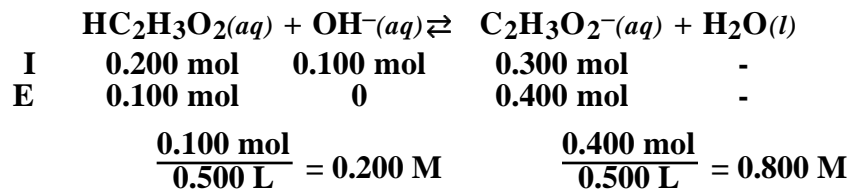
$$1.2 \times 10^{-5} \text{ M} = x = [\text{H}^+]$$

$$\text{pH} = 4.92$$

When the NaOH is added to the solution we must convert to moles of the weak acid and conjugate base.

$$0.400 \frac{\text{mol HC}_2\text{H}_3\text{O}_2}{\text{L}} \cdot 0.500 \text{ L} = 0.200 \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$0.600 \frac{\text{mol HC}_2\text{H}_3\text{O}_2}{\text{L}} \cdot 0.500 \text{ L} = 0.300 \text{ mol C}_2\text{H}_3\text{O}_2^-$$



$$K_a = \frac{[C_2H_3O_2^-][H^+]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{(0.800 + x)(1 \times 10^{-7} + x)}{(0.200 - x)} \quad x < 0.350$$

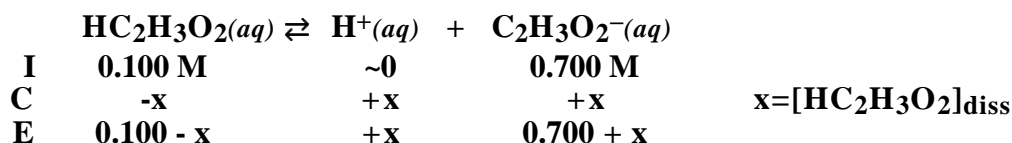
$$1.8 \times 10^{-5} = \frac{0.800(x)}{0.200}$$

$$4.5 \times 10^{-6} M = x = [H^+]$$

$$pH = 5.35$$

The change is 0.43 pH units

c) 500 mL of 0.100 M $HC_2H_3O_2$ and 0.700 M $NaC_2H_3O_2$



$$K_a = \frac{[C_2H_3O_2^-][H^+]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{(0.700 + x)(x)}{(0.100 - x)} \quad x < 0.600$$

$$1.8 \times 10^{-5} = \frac{0.700(x)}{0.100}$$

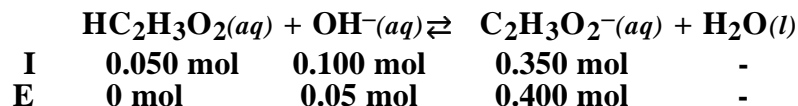
$$2.6 \times 10^{-6} M = x = [H^+]$$

$$pH = 5.59$$

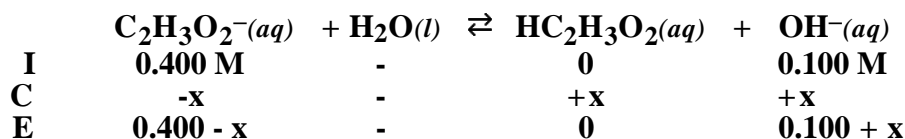
When the NaOH is added to the solution we must convert to moles of the weak acid and conjugate base.

$$0.100 \frac{\text{mol } HC_2H_3O_2}{L} \cdot 0.500 L = 0.050 \text{ mol } HC_2H_3O_2$$

$$0.700 \frac{\text{mol } HC_2H_3O_2}{L} \cdot 0.500 L = 0.350 \text{ mol } C_2H_3O_2^-$$



$$\frac{0.050 \text{ mol}}{0.500 L} = 0.100 M [OH^-] \quad \frac{0.400 \text{ mol}}{0.500 L} = 0.800 M$$



$$K_b = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$$5.5 \times 10^{-10} = \frac{[x][.100 + x]}{[0.400 - x]} \quad x \ll 0.100$$

$$2.2 \times 10^{-9} = x$$

$$[OH^-] = 0.100 + x = 0.100 + 2.2 \times 10^{-9} = 0.100 M$$

$$pOH = 1.00 \text{ and } pH = 13$$

The change is 7.41 pH units

