Chemistry 146 Lecture Problems
Acetic acid titration

Starting with the following solution of acetic acid: $M := mole \cdot liter^{-1}$

$K_a := 1.79 \cdot 10^{-5} \cdot M$

$C_{acid} := 0.100 \cdot M$

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

$mole_{acid} := C_{acid} \cdot V_{acid}$ $\quad mole_{acid} = 0.01 \circ mole$

First Calculate the initial equlibrium and pH according to the reaction

$CH_3COOH + H_2O$ <-> CH_3COO^- + H_3O^+

$(C_{acid} - X)$ $\quad X \quad X$

Equlibrium Expression: $K_a = \frac{C_{CH3COO} \cdot C_{H3O}}{C_{CH3COOH}}$

Substitute Variables: $K_a = \frac{X \cdot X}{C_{acid} - X}$

Substitute Values: $1.79 \cdot 10^{-5} \cdot M = \frac{X^2}{0.100 \cdot M - X}$

Simplify: $1.79 \cdot 10^{-5} \cdot M = \frac{X^2}{0.100 \cdot M}$

Rearange: $X := \sqrt{(1.79 \cdot 10^{-5}) \cdot 0.100 \cdot M^2}$

Solve: $X = 1.33791 \cdot 10^{-3} \circ M$

This gives equlibrium conditions as:

$C_{CH3COOH} := C_{acid} - X$ $\quad C_{CH3COOH} = 0.09866 \circ M$

$C_{CH3COO} := X$ $\quad C_{CH3COO} = 1.33791 \cdot 10^{-3} \circ M$

$C_{H3O} := X$ $\quad C_{H3O} = 1.33791 \cdot 10^{-3} \circ M$

$pH := -1 \cdot \log\left(\frac{C_{H3O}}{M}\right)$ $\quad pH = 2.87357$

$pOH := 14 - pH$ $\quad pOH = 11.12643$

Add a small amount of NaOH.

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

First since OH^- is a strong base, and acetic acid is the strongest acid available,

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

This reaction will go to completion so that for:

$C_{NaOH} := 0.1 \cdot M$

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

$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH}$ $\qquad mole_{NaOH} = 1 \cdot 10^{-4} \cdot mole$

$V_{total} := V_{acid} + V_{NaOH}$ $\qquad V_{total} = 0.101 \cdot liter$

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

Acetic acid

$mole_{CH3COOH} := mole_{acid} - mole_{NaOH}$

$$C_{CH3COOH} := \frac{(mole_{CH3COOH})}{V_{total}}$$

$C_{CH3COOH} = 9.802 \cdot 10^{-2} \cdot M$

Acetate Ions

$mole_{CH3COO} := mole_{NaOH}$

$$C_{CH3COO} := \frac{(mole_{CH3COO})}{V_{total}}$$

$C_{CH3COO} = 9.90099 \cdot 10^{-4} \cdot M$

Based upon these initial concentrations, solve for the equlibrium values, assuming X reacts. Since the initial concentration of the conjugate base is very small, no assumptions are appropriate:

$$1.79 \cdot 10^{-5} = \frac{(9.901 \cdot 10^{-4} + X) \cdot X}{9.802 \cdot 10^{-2} - X}$$

expands to $$1.79 \cdot 10^{-5} = \frac{(9.901 \cdot 10^{-4} \cdot X + X^2)}{9.802 \cdot 10^{-2} - X}$$

rearanges to $$1.79 \cdot 10^{-5} \cdot (9.802 \cdot 10^{-2} - X) - (9.901 \cdot 10^{-4} \cdot X + X^2) = 0$$

simplifies to $$1.754558 \cdot 10^{-6} - 1.008 \cdot 10^{-3} \cdot X - 1. \cdot X^2 = 0$$

has solution(s) $$X := \begin{bmatrix} -1.9212416872220489408 \cdot 10^{-3} \\ 9.1324168722204894 08 \cdot 10^{-4} \end{bmatrix}$$

If we had made the assumption that X was small, would it work?

Select the appropriate root:

$$X := 9.1324 \cdot 10^{-4} \cdot M$$

Now from the non-equlibrium concentrations above where:

$C_{CH3COOH} = 0.09802 \cdot M$ $\qquad$ $C_{CH3COO} = 9.90099 \cdot 10^{-4} \cdot M$

The equlibrium concentrations (Without the Henderson Hasselbach approximation)

$C_{CH3COOH} := C_{CH3COOH} - X$ $\qquad$ $C_{CH3COOH} = 0.09711 \cdot M$

$C_{CH3COO} := C_{CH3COO} + X$ $\qquad$ $C_{CH3COO} = 1.90334 \cdot 10^{-3} \cdot M$

$C_{H3O} := X$ $\qquad$ $C_{H3O} = 9.1324 \cdot 10^{-4} \cdot M$

This gives a pH for the solution:

$pH := -\log\left(\frac{C_{H3O}}{M}\right)$ $\qquad$ $pH = 3.03942$

$pOH := 14 - pH$ $\qquad$ $pOH = 10.96058$

Add more NaOH.

$C_{NaOH} = 0.1 \cdot M$ $\quad$ $V_{NaOH} := 10 \cdot mL$

$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH}$ $\quad$ $mole_{NaOH} = 1 \cdot 10^{-3} \cdot mole$

$V_{total} := V_{acid} + V_{NaOH}$ $\quad$ $V_{total} = 110 \cdot mL$

The new initial, NON EQULIBRIUM, conditions are:

Acetic acid

$mole_{CH3COOH} := mole_{acid} - mole_{NaOH}$

$$C_{CH3COOH} := \frac{(mole_{CH3COOH})}{V_{total}}$$

$C_{CH3COOH} = 8.1818 \cdot 10^{-2} \cdot M$

Acetate Ions

$mole_{CH3COO} := mole_{NaOH}$

$$C_{CH3COO} := \frac{(mole_{CH3COO})}{V_{total}}$$

$C_{CH3COO} = 9.09091 \cdot 10^{-3} \cdot M$

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

$$K_a = \frac{(C_{CH3COO} + X) \cdot X}{C_{CH3COOH} - X}$$

Assume X is small and simplify: $$K_a = \frac{C_{CH3COO} \cdot X}{CH_{CH3COOH}}$$

Rearanges to: $$X := \frac{K_a}{C_{CH3COO}} \cdot C_{CH3COOH}$$

Solve: $X = 1.611 \cdot 10^{-4} \cdot M$

This gives the following equlibrium concentraitons:

$C_{CH3COOH} := C_{CH3COOH} - X$ $\quad$ $C_{CH3COOH} = 0.08166 \cdot M$

$C_{CH3COO} := C_{CH3COO} + X$ $\quad$ $C_{CH3COO} = 9.25201 \cdot 10^{-3} \cdot M$

$C_{H3O} := X$ $\quad$ $C_{H3O} = 1.611 \cdot 10^{-4} \cdot M$

$pH := -\log\left(\frac{C_{H3O}}{M}\right)$ $\quad$ $pH = 3.7929$

$pOH := 14 - pH$ $\quad$ $pOH = 10.2071$

Since [H3O+] is much smaller than the buffer concentrations, this answer is acceptable.

Add enough NaOH to use up half of the acetic acid.

$C_{NaOH} = 0.1 \cdot M$

$V_{NaOH} := 50 \cdot mL$

$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH}$ $\quad mole_{NaOH} = 5 \cdot 10^{-3} \cdot mole$

$V_{total} := V_{acid} + V_{NaOH}$ $\quad V_{total} = 0.15 \cdot liter$

The new initial, NON EQULIBRIUM, conditions are:

Acetic acid

$mole_{CH3COOH} := mole_{acid} - mole_{NaOH}$

$$C_{CH3COOH} := \frac{(mole_{CH3COOH})}{V_{total}}$$

$C_{CH3COOH} = 3.3333 \cdot 10^{-2} \cdot M$

Acetate Ions

$mole_{CH3COO} := mole_{NaOH}$

$$C_{CH3COO} := \frac{(mole_{CH3COO})}{V_{total}}$$

$C_{CH3COO} = 3.3333 \cdot 10^{-2} \cdot M$

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

$$K_a = \frac{(C_{CH3COO} + X) \cdot X}{C_{CH3COOH} - X}$$

Assume X is small and simplify: $\quad K_a = \frac{C_{CH3COO} \cdot X}{CH_{CH3COOH}}$

Rearanges to: $\quad X := \frac{K_a}{C_{CH3COO}} \cdot C_{CH3COOH}$

Solve: $\quad X = 1.79 \cdot 10^{-5} \cdot M$

This gives the following equlibrium concentraitons:

$C_{CH3COOH} := C_{CH3COOH} - X$ $\quad C_{CH3COOH} = 0.03332 \cdot M$

$C_{CH3COO} := C_{CH3COO} + X$ $\quad C_{CH3COO} = 0.03335 \cdot M$

$C_{H3O} := X$ $\quad C_{H3O} = 1.79 \cdot 10^{-5} \cdot M$

$pH := -\log\left(\frac{C_{H3O}}{M}\right)$ $\quad pH = 4.74715$

$pOH := 14 - pH$ $\quad pOH = 9.25285$

Since [H3O+] is smaller than the buffer concentrations, this answer is acceptable.

Add more NaOH.

$C_{NaOH} := 0.1 \cdot M$

$V_{NaOH} := 75 \cdot mL$

$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH}$ $\quad mole_{NaOH} = 7.5 \cdot 10^{-3} \, mole$

$V_{total} := V_{acid} + V_{NaOH}$ $\quad V_{total} = 0.175 \, liter$

The new initial, NON EQULIBRIUM, conditions are:

Acetic acid

$mole_{CH3COOH} := mole_{acid} - mole_{NaOH}$

$C_{CH3COOH} := \frac{(mole_{CH3COOH})}{V_{total}}$

$C_{CH3COOH} = 1.4286 \cdot 10^{-2} \, M$

Acetate Ions

$mole_{CH3COO} := mole_{NaOH}$

$C_{CH3COO} := \frac{(mole_{CH3COO})}{V_{total}}$

$C_{CH3COO} = 4.2857 \cdot 10^{-2} \, M$

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

$$K_a = \frac{(C_{CH3COO} + X) \cdot X}{C_{CH3COOH} - X}$$

Assume X is small and simplify: $K_a = \frac{C_{CH3COO} \cdot X}{CH_{CH3COOH}}$

Rearanges to: $X := \frac{K_a}{C_{CH3COO}} \cdot C_{CH3COOH}$

Solve: $X = 5.96667 \cdot 10^{-6} \, M$

This gives the following equlibrium concentraitons:

$C_{CH3COOH} := C_{CH3COOH} - X$ $\quad C_{CH3COOH} = 0.01428 \, M$

$C_{CH3COO} := C_{CH3COO} + X$ $\quad C_{CH3COO} = 0.04286 \, M$

$C_{H3O} := X$ $\quad C_{H3O} = 5.96667 \cdot 10^{-6} \, M$

$pH := -\log\left(\frac{C_{H3O}}{M}\right)$ $\quad pH = 5.22427$

$pOH := 14 - pH$ $\quad pOH = 8.77573$

Since [H3O+] is smaller than the buffer concentrations, this answer is acceptable.

Add enough NaOH to use up all the CH_3COOH available.

This is the equlvilance point for the titration. The major species in the solution is CH_3COO^-
Since this is the conjugate base to a weak acid the pH is calculated as for a solution of this base for the reaction:

$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

$C_{NaOH} := 0.1 \cdot M$

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

$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH}$ $\quad mole_{NaOH} = 0.01 \cdot mole$

$V_{total} := V_{acid} + V_{NaOH}$ $\quad V_{total} = 0.2 \cdot liter$

Since the NaOH is a strong base the initial NON-EQULIBRIUM conditions are:

Acetate ion

$mole_{CH3COO} := mole_{NaOH}$

$mole_{CH3COO} = 0.01 \cdot mole$

$C_{CH3COO} := \frac{mole_{acid}}{V_{total}}$

$C_{CH3COO} = 0.05 \cdot M$

Acetic acid

$mole_{CH3COOH} := mole_{acid} - mole_{NaOH}$

$mole_{CH3COOH} = 0 \cdot mole$

$C_{CH3COOH} := 0$

The EQULIBRIUM expression for this base reaction above is:

$$K_b = \frac{C_{CH3COOH} \cdot C_{OH}}{C_{CH3COO}}$$

From the balanced equation, this is:

$$K_b = \frac{X^2}{C_{CH3COO} - X}$$

Find K_b:

Since: $\quad K_w = K_b \cdot K_a$

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

$K_a = 1.79 \cdot 10^{-5} \cdot M$

Rearange $\quad K_b := \frac{K_w}{K_a}$

Solve for K_b $\quad K_b = 5.58659 \cdot 10^{-10} \cdot M$

Substituting into the equlibrium expression:

$$5.5556\cdot10^{-10}\cdot M = \frac{X^2}{0.05\cdot M - X}$$

Assume that X is small compared to the buffer and the equation rearanges to:

$$X := \sqrt{2.7778\cdot10^{-11}\cdot M^2}$$

$$X = 5.27048\cdot10^{-6} M$$

NOTE: without assuming that X is very small the equation solves for X:

$$X := \begin{bmatrix} 5.2702060760763781548\cdot10^{-6}\cdot M \\ -5.2707616360763781548\cdot10^{-6}\cdot M \end{bmatrix}$$

Select the physically meaningful root gives:

$$X := 5.2702060760763781548\cdot10^{-6}\cdot M$$

This is identical to the above answer.

This gives equlibrium concentrations as:

$$C_{CH3COO} := C_{CH3COO} - X \qquad C_{CH3COO} = 0.04999 M$$

$$C_{CH3COOH} := X \qquad C_{CH3COOH} = 5.27021\cdot10^{-6} M$$

$$C_{OH} := X \qquad C_{OH} = 5.27021\cdot10^{-6} M$$

From this the pOH and pH

$$pOH := -\log\left(\frac{C_{OH}}{M}\right) \qquad pOH = 5.27817$$

$$pH := 14 - pOH \qquad pH = 8.72183$$

Note: the equlvilance point
for this titration is NOT at pH 7.

Add excess NaOH.

Since the excess OH^- is a strong base present it will determine the pH

$$C_{NaOH} = 0.1 \cdot M$$

$$V_{NaOH} := 110 \cdot mL$$

$$mole_{NaOH} := C_{NaOH} \cdot V_{NaOH} \qquad mole_{NaOH} = 0.011 \cdot mole$$

$$V_{total} := V_{acid} + V_{NaOH} \qquad V_{total} = 0.21 \cdot liter$$

First OH^- will convert all the CH_3COOH to $CH3COO^-$ these initial conditions are:

$$mole_{CH3COOH} := 0$$

$$mole_{CH3COO} := mole_{acid}$$

Calculate the [OH-], from the excess OH.

$$mole_{OH} := mole_{NaOH} - mole_{acid} \qquad mole_{OH} = 1 \cdot 10^{-3} \cdot mole$$

$$C_{OH} := \frac{mole_{OH}}{V_{total}} \qquad C_{OH} = 4.7619 \cdot 10^{-3} \cdot M$$

Then use this to calculate pOH and pH:

$$pOH := -\log\left(\frac{C_{OH}}{M}\right) \qquad pOH = 2.32222$$

$$pH := 14 - pOH \qquad pH = 11.67778$$

Finish off with a table of the above results:

mL NaOH added	pH	(approximation)	pOH	(approximation)
0	2.87		11.13	
1	3.04	(2.75)	10.96	(11.25)
10	3.80	(3.79)	10.20	(10.21)
50	4.74	(4.74)	9.25	(9.25)
100	8.72	(8.72)	5.28	(5.28)
110	11.68	(11.68)	2.32	(2.32)