

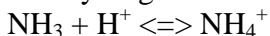
AP* Buffer Equilibrium Free Response Questions KEY

Essay Questions

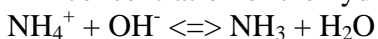
1972

Since ammonium chloride is a salt of a weak base, the weak base is needed, ammonia, NH_3 .

(a) When moderate amounts of a strong acid, H^+ , are added, the ammonia reacts with it. The concentration of the hydrogen ion remains essentially the same and therefore only a very small change in pH.



(b) When moderate amounts of a strong base, OH^- , are added, the ammonium ion reacts with it. The concentration of the hydrogen ion remains essentially the same and therefore only a very small change in pH.



(c) By diluting with water the relative concentration ratio of $[\text{NH}_4^+]/[\text{NH}_3]$ does not change, therefore there should be no change in pH.

1983

(a) three points

A buffer solution resists changes in pH upon the addition of an acid or base.

Preparation:

- Mix a weak acid + a salt of a weak acid.
- Or mix a weak base + a salt of a weak base.
- Or mix a weak acid with about half as many moles of strong base.
- Or mix a weak base with about half as many moles of strong acid.
- Or mix a weak acid and a weak base.

(b) five points

Carla has the correct procedure. She has mixed a weak base, NH_3 , with the salt of a weak base, NH_4Cl . Archie has buffer solution but it has a pH around 5.

Beula does not have a buffer solution, since her solution consists of a strong acid and a salt of a weak base.

Dexter does not have a buffer solution, since his solution consists of a weak base plus a strong base.

1988

Average score = 1.76

a) two points

The sharp vertical rise in the pH on the pH-volume curve appears at the equivalence point (about 23 mL). Because the acid is monoprotic, the number of moles of acid equals the number of moles of NaOH. That number is the product of the exact volume and the molarity of the NaOH. The molarity of the acid is the number of moles of the acid divided by 0.030 L, the volume of the acid.

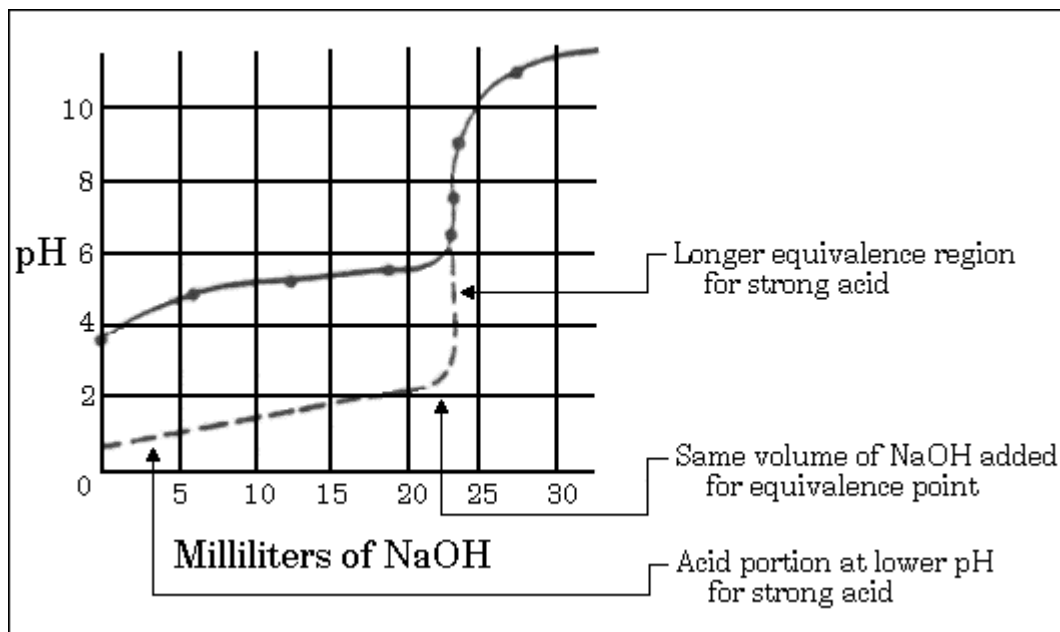
b) two points

At the half-equivalence point (where the volume of the base added is exactly half its volume at the equivalence point), the concentration $[HX]$ of the weak acid equals the concentration $[X^-]$ of its anion. Thus, in the equilibrium expression, $[H^+][X^-] / [HX] = K_a$. Therefore, pH at the half-equivalence point equals pK_a

c) one point

Cresol red is the best indicator because its pK_a (about 8) appears midway in the steep equivalence region. This insures that at the equivalence point the maximum color change for the minimal change in the volume of NaOH added is observed.

d) three points



1992

6 (a) Best conjugate pair: H_2PO_4^- , HPO_4^{2-} (1)
 - pts when $7.2 = \text{pH} = \text{pKa}$ for this pair when $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$ (1)

(b) Dissolve equal moles (or amounts) of H_2PO_4^- and (1)
 pt HPO_4^{2-} (or appropriate compounds) in water

If answer in (a) was HCO_3^- , CO_3^{2-} , students would receive
 1 pt in (b) if they stated that $\text{CO}_3^{2-}/\text{HCO}_3^-$ mole ratio was 6.7:1

(c) pH not change (1)
 Capacity of buffer would increase because (1)
 3 pts there are more moles of conjugate acid and (1)
 conjugate base to react with added base or acid

(d) Add strong base to salt of conjugate acid (1)
 2 pts or add strong acid to salt of conjugate base
 Add 1 mole conjugate acid to $\frac{1}{2}$ mole strong base (1)
 or 1 mole conjugate base to $\frac{1}{2}$ mole strong acid

or use pH meter to monitor addition of
 strong base to conjugate acid
or strong acid to conjugate base

1998

Question 5
(8 points)

- (a) 4 essential steps: 2 pts
- 1) weigh KHP
 - 2) fill buret with NaOH solution
 - 3) add indicator (phenolphthalein)
 - 4) titrate to endpoint (color change)

- Two points earned for all 4 steps; one point earned for 2 or 3 steps
- Titration of acid into base accepted if described correctly

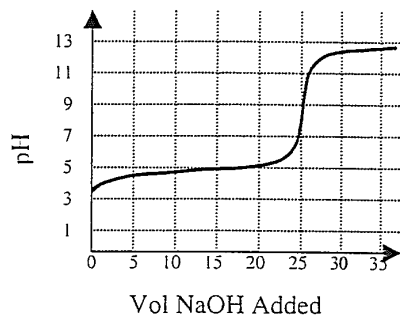
(b) $\text{moles KHP} = \frac{\text{mass KHP}}{\text{molar mass KHP}}$ 1 pt

$\text{moles KHP} = \text{moles OH}^- \text{ at equivalence and } \frac{\text{moles OH}^-}{\text{liters NaOH}} = [\text{OH}^-]$ 1 pt

- Acceptable if some parts of part (b) appear in (a)

- (c) Curve should have 3 important features:
- 1) curve begins above pH 1, but below pH 7
 - 2) equivalence point at 25 mL
 - 3) equivalence point above pH 7

- Both points earned for all 3 features
- One point earned for any 2 of the 3 features

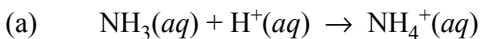


- (d) At the half-way point in the titration, $\text{pH} = \text{p}K_a$. 1 pt

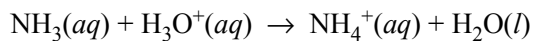
- (e) At point A in the titration, the anion in highest concentration is Y^{2-} . 1 pt
- Also accepted: Y^{-2} , Y^- , $\text{Y}^=$, and specific anions such as SO_4^{2-} , SO_3^{2-}
 - HY^- , Y^- , and "Y ion" not accepted

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Question 8 (8 points)



or

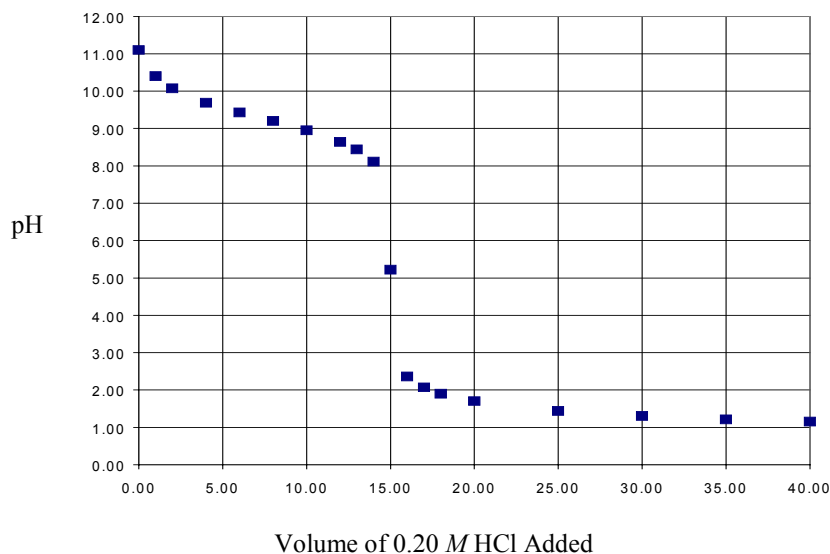


1 pt.

Note: phase designations not required to earn point

(b) Sketch of Titration Curve:

3 pts.



- 1st pt. ⇒ initial pH must be > 7 (calculated pH ≈ 11)
- 2nd pt. ⇒ equivalence point occurs at 15.0 mL ± 1 mL of HCl added (equivalence point must be detectable from the shape of the curve or a mark on the curve)
- 3rd pt. ⇒ pH at equivalence point must be < 7 (calculated pH ≈ 5).

Note: a maximum of 1 point earned for any of the following:

- a line without an equivalence point
- a random line that goes from high pH to low pH
- an upward line with increasing pH (equivalence point MUST be at 15.0 mL)

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Question 8
(continued)

- (c) Methyl Red would be the best choice of indicator, **1 pt.**
because

the pK_a for Methyl Red is closest to the pH at the equivalence point. **1 pt.**

Notes:

- explanation must agree with equivalence point on graph
- alternative explanation that titration involves strong acid and weak base (with product an acidic salt) earns the point

- d) The resulting solution is basic. **1 pt.**

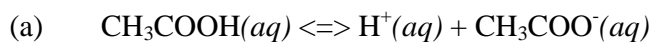
K_b for NH_3 (1.8×10^{-5}) and K_a for NH_4^+ (5.6×10^{-10}) indicate that NH_3 is a stronger base than NH_4^+ is an acid

or **1 pt.**

$[\text{OH}^-] = K_b = 1.8 \times 10^{-5}$ because of the equimolar and equivolume amounts of ammonium and ammonia \Rightarrow cancellation in the buffer pH calculation. Thus $\text{pOH} \approx 5$ and $\text{pH} \approx 9$ (i.e., recognition of buffer, so that $\log\left(\frac{0.05}{0.05}\right) = 0 \Rightarrow \text{pOH} = \text{p}K_b \approx 5 \Rightarrow \text{pH} = 14 - \text{pOH} \approx 9$)

Problems

1970



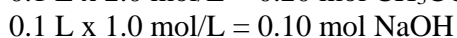
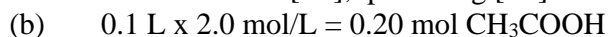
$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = X$$

$$[\text{CH}_3\text{COOH}] = 2.0 - X, X \ll 2.0, (2.0 - X) = 2.0$$

$$1.8 \times 10^{-5} = \frac{X^2}{2.0}$$

$$X = 6.0 \times 10^{-3} = [\text{H}^+]; \text{pH} = -\log [\text{H}^+] = 2.22$$



the 0.10 mol of hydroxide neutralizes 0.10 mol CH_3COOH with 0.10 mol remaining with a concentration of $0.10 \text{ mol}/0.20 \text{ L} = 0.5 \text{ M}$. This also produces 0.10 mol of acetate ion in 0.20 L, therefore, $[\text{CH}_3\text{COO}^-] = 0.50 \text{ M}$.

$$1.8 \times 10^{-5} = \frac{[\text{H}^+][0.50]}{[0.50]}$$

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

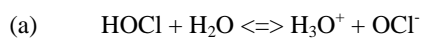


$$= 0.50 \text{ M} \times \frac{0.040 \text{ L}}{0.14 \text{ L}} = 0.143 \text{ M}$$

$$[\text{H}^+]_o = 0.50 \text{ M} \times \frac{0.14 \text{ L}}{0.14 \text{ L}} = 0.357 \text{ M}$$

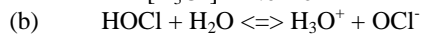
the equilibrium will be pushed nearly totally to the left resulting in a decrease of the hydrogen ion by 0.143M. Therefore, the $[\text{H}^+]_{\text{eq}} = 0.357 \text{ M} - 0.143 \text{ M} = 0.214 \text{ M}$.

1977



$$3.2 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{X^2}{(0.050 - X)}$$

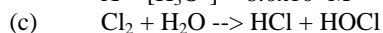
$$X = [\text{H}_3\text{O}^+] = 4.0 \times 10^{-5} \text{ M}$$



$$\frac{[\text{H}_3\text{O}^+][0.010 + X]}{[0.0250 - X]} = 3.2 \times 10^{-8}$$

$$; X \ll 0.010$$

$$X = [\text{H}_3\text{O}^+] = 8.0 \times 10^{-8} \text{ M}$$



$$[\text{HOCl}] = [\text{HCl}] = 0.0040 \text{ M}$$

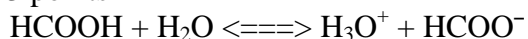
HCl as principal source of H_3O^+

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.40$$

AP* Acid-Base Buffer Free Response Questions KEY

1982

a) 3 points



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

	[HCOOH]	[H ₃ O ⁺]	[HCOO ⁻]
Initial:	0.40		0.60
Equil:	0.40 - y	y	0.60 + y

$$K_a = 1.8 \times 10^{-4} = \frac{y(0.40 + y)}{0.60 - y}$$

neglect the +y and the -y

$$[\text{H}_3\text{O}^+] = y = 1.2 \times 10^{-4}$$

$$\text{pH} = -\log(1.2 \times 10^{-4}) = 3.92$$

Alternative Approach:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= -\log(1.8 \times 10^{-4}) + \log(0.40 / 0.60)$$

$$= 3.92$$

b) 1 point

The pH remains unchanged because the ratio of the formate and formic acid stays the same

c) 3 points

Initial amounts of concentrations:

$$1.00 \text{ M HCl} \times 0.00500 \text{ L} = 0.00500 \text{ mole HCl}$$

$$0.40 \text{ M HCOOH} \times 0.100 \text{ L} = 0.040 \text{ mole HCOOH}$$

$$0.60 \text{ M HCOO}^- \times 0.100 = 0.060 \text{ mole HCOO}^-$$

or

$$1.00 \text{ M HCl} \times (5.00 \text{ ml} / 105 \text{ ml}) = 0.0476 \text{ M HCl}$$

$$0.40 \text{ M HCOOH} \times (100 \text{ ml} / 105 \text{ ml}) = 0.38 \text{ M HCOOH}$$

$$0.60 \text{ M HCOO}^- \times (100 \text{ ml} / 105 \text{ ml}) = 0.57 \text{ M HCOO}^-$$

Amounts or concentrations after H⁺ reacts with HCOO⁻ :

$$0.040 + 0.005 = 0.045 \text{ mole HCOOH}$$

$$0.060 - 0.005 = 0.055 \text{ mole HCOO}^-$$

or

$$0.43 \text{ M HCOOH and } 0.52 \text{ M HCOO}^-$$

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-4} \times \left(\frac{0.045/\text{vol.}}{0.055/\text{vol.}} \right) = 1.5 \times 10^{-4} \text{ M}$$

d) 2 points

$$0.800 \text{ liter} \times 2.00 \text{ M HCOOH} = 1.60 \text{ moles HCOOH}$$

$$0.200 \text{ liter} \times 4.80 \text{ M NaOH} = 0.96 \text{ mole OH}^-$$

1.60 moles HCOOH + 0.96 mole OH⁻ yields 0.64 mole HCOOH and 0.96 mole HCOO⁻

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-4} \times \frac{0.64 \text{ mole/liter}}{0.96 \text{ mole/liter}} = 1.2 \times 10^{-4}$$

The alternative approach in part (a) can also be used in part (d)

1984

Average score 4.36

a) two points

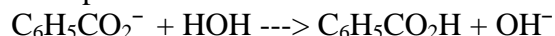
$$\text{pH} = 8.60$$

$$[\text{H}^+] = 1 \times 10^{-8.60} \text{ M} = 2.5 \times 10^{-9} \text{ M}$$

$$[\text{OH}^-] = (1 \times 10^{-14}) / (2.5 \times 10^{-9}) \text{ M}$$

$$= 4.0 \times 10^{-6} \text{ M}$$

b) three points

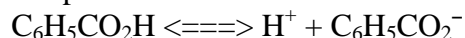


$$K = \frac{[\text{C}_6\text{H}_5\text{CO}_2\text{H}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{CO}_2^-]}$$

$$= \frac{(4.0 \times 10^{-8})(4.0 \times 10^{-6})}{(0.10 - 4.0 \times 10^{-6})}$$

$$= 1.6 \times 10^{-10}$$

c) one point

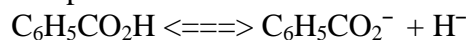


$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]}$$

$$= \frac{(2.5 \times 10^{-9})(0.10)}{(4.0 \times 10^{-6})}$$

$$= 6.3 \times 10^{-5}$$

d) two points



$$\text{pH} = 2.88$$

$$[\text{H}^+] = 1 \times 10^{-2.88} \text{ M} = 1.3 \times 10^{-3}$$

$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]}$$

$$6.3 \times 10^{-5} = \frac{(1.3 \times 10^{-3})(1.3 \times 10^{-3})}{x}$$

$$x = 2.8 \times 10^{-2} \text{ M}$$

Total $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ in solution =

$$(2.8 \times 10^{-2} + 1.3 \times 10^{-3}) \text{ M} =$$

$$2.9 \times 10^{-2} \text{ M}$$

1991

a) three points

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

$$1.3 \times 10^{-5} = \frac{x^2}{0.20}$$

$$x = [\text{H}^+] = 1.6 \times 10^{-3}$$

b) one point

$$\% \text{ dissociation} = \frac{[\text{H}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$= \frac{1.6 \times 10^{-3}}{0.20} = 0.80\%$$

c) two points

$$[\text{H}^+] = \text{antilog}(-5.20) = 6.3 \times 10^{-6}$$

$$1.3 \times 10^{-5} = (6.3 \times 10^{-6}) \times ([\text{C}_3\text{H}_5\text{O}_2^-] \div [\text{HC}_3\text{H}_5\text{O}_2])$$

$$[\text{C}_3\text{H}_5\text{O}_2^-] \div [\text{HC}_3\text{H}_5\text{O}_2] = 1.3 \times 10^{-5} \div 6.3 \times 10^{-6} = 2.1$$

An alternate solution for (c) based on the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_a + \log([\text{base}] \div [\text{acid}])$$

$$5.20 = 4.89 + \log([\text{C}_3\text{H}_5\text{O}_2^-] \div [\text{HC}_3\text{H}_5\text{O}_2])$$

$$\log([\text{C}_3\text{H}_5\text{O}_2^-] \div [\text{HC}_3\text{H}_5\text{O}_2]) = 0.31$$

$$[\text{C}_3\text{H}_5\text{O}_2^-] \div [\text{HC}_3\text{H}_5\text{O}_2] = 2.0$$

d) six points

$$0.10 \text{ L} \times 0.35 \text{ mol/L} = 0.035 \text{ mol HC}_3\text{H}_5\text{O}_2$$

$$0.10 \text{ L} \times 0.50 \text{ mol/L} = 0.050 \text{ mol C}_3\text{H}_5\text{O}_2^-$$

$$0.035 \text{ mol} - 0.004 \text{ mol} = 0.031 \text{ mol HC}_3\text{H}_5\text{O}_2$$

$$0.050 \text{ mol} + 0.004 \text{ mol} = 0.054 \text{ mol C}_3\text{H}_5\text{O}_2^-$$

$$1.3 \times 10^{-5} = [\text{H}^+] \times [(0.054 \text{ mol}/0.1 \text{ L}) \div (0.031 \text{ mol}/0.1 \text{ L})]$$

Can use 0.54 and 0.31 instead.

$$[\text{H}^+] = 7.5 \times 10^{-6}$$

$$\text{pH} = 5.13$$

An alternate solution for (d) based on the Henderson-Hasselbalch equation.

use []s or moles of $\text{HC}_3\text{H}_5\text{O}_2$ and $\text{C}_3\text{H}_5\text{O}_2^-$

$$\text{pH} = \text{pK}_a + \log(0.054 / 0.031)$$

$$= 4.89 + 0.24 = 5.13$$

1996

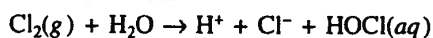
QUESTION 2*(9 points)*

2.



Hypochlorous acid, HOCl, is a weak acid commonly used as a bleaching agent. The acid-dissociation constant, K_a , for the reaction represented above is 3.2×10^{-8} .

- Calculate the $[\text{H}^+]$ of a 0.14-molar solution of HOCl.
- Write the correctly balanced net ionic equation for the reaction that occurs when NaOCl is dissolved in water and calculate the numerical value of the equilibrium constant for the reaction.
- Calculate the pH of a solution made by combining 40.0 milliliters of 0.14-molar HOCl and 10.0 milliliters of 0.56-molar NaOH.
- How many millimoles of solid NaOH must be added to 50.0 milliliters of 0.20-molar HOCl to obtain a buffer solution that has a pH of 7.49? Assume that the addition of the solid NaOH results in a negligible change in volume.
- Household bleach is made by dissolving chlorine gas in water, as represented below.



Calculate the pH of such a solution if the concentration of HOCl in the solution is 0.065 molar.

Scoring Guide

General Notes: All simplifying assumptions are justified within 5%.

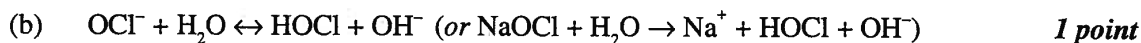
One point deduction for a significant figure or math error, applied only once per problem.

No credit earned for numerical answer without justification.

(a) $[\text{H}^+] = [\text{OCl}^-] \approx \sqrt{0.14 \times 3.2 \times 10^{-8}} = 6.7 \times 10^{-5} \text{ M}$ **2 points**

$$\text{since } K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \approx \frac{[\text{H}^+]^2}{c_{\text{HOCl}}}$$

(Note: 1 point for correct substitutions; 1 point for computation)



$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{3.2 \times 10^{-8}} = 3.1 \times 10^{-7}$$
 1 point

(c) Concentrations before reaction: $[\text{HOCl}] = \frac{(0.0400)(0.14)}{(0.050)} = 0.11 \text{ M}$
 $[\text{OH}^-] = \frac{(0.0100)(0.56)}{(0.050)} = 0.11 \text{ M}$

Thus reaction is essentially complete and \equiv solution of NaOCl
 and $[\text{OCl}^-] \approx 0.11 \text{ M}$ (or reaction is at equivalence point)

1 point

Then $[\text{OH}^-] \approx [\text{HOCl}] \Rightarrow K_b = \frac{[\text{OH}^-]^2}{0.11} = 3.1 \times 10^{-7} \Rightarrow$

$[\text{OH}^-] = \sqrt{(0.11)(3.1 \times 10^{-7})} = 1.8 \times 10^{-4}$, pOH = 3.73
 pH = 14 - 3.73 = 10.27

1 point

(d) pH = 7.49 \Rightarrow $[\text{H}^+] = 3.2 \times 10^{-8}$
 pH = pK_a, or $[\text{H}^+] = K_a$.

So $\frac{[\text{OCl}^-]}{[\text{HOCl}]} = 1$, or solution must be half neutralized

1 point

initial mmol HOCl = 50.0 \times 0.20 = 10.0 mmol

mmol NaOH required = $\frac{10.0}{2} = 5.0 \text{ mmol}$

1 point

(e) From equation, 1 mol H⁺ produced for each 1 mole of HOCl produced,
 thus $[\text{H}^+] \approx [\text{HOCl}] = 0.065 \text{ M} \Rightarrow$ pH = 1.19

1 point

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2001 SCORING GUIDELINES

Question 3

(10 points)

(a) $(0.325 \text{ g}/2.00 \text{ g}) \times 100\% = \mathbf{16.2\%}$ *1 point*

(b) $\frac{1.200 \text{ g H}_2\text{O}}{18.02 \text{ g/mol}} = 0.06659 \text{ mol H}_2\text{O}$

$(0.06659 \text{ mol H}_2\text{O})(2 \text{ mol H/mol H}_2\text{O}) = 0.1332 \text{ mol H}$

$(0.1332 \text{ mol H})(1.008 \text{ g/mol H}) = \mathbf{0.1343 \text{ g H}}$ *1 point*

$n_{\text{CO}_2} = \frac{PV}{RT} = \frac{(750/760) \text{ atm} \times 3.72 \text{ L}}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = \mathbf{0.150 \text{ mol CO}_2}$ *1 point*

$(0.150 \text{ mol CO}_2)(1 \text{ mol C/mol CO}_2) = 0.150 \text{ mol C}$

$(0.150 \text{ mol C})(12.0 \text{ g/mol}) = \mathbf{1.80 \text{ g C}}$ *1 point*

grams of oxygen = $3.00 \text{ g} - (1.80 \text{ g} + 0.133 \text{ g}) = \mathbf{1.07 \text{ g O}}$ *1 point*

Note: The first point is earned for getting the correct mass of H ; the second point is earned for using the Ideal Gas Law and substituting consistent values of P , V , R , and T . The third point is earned for converting moles of CO_2 to moles of C and then grams of C. If the number of moles of CO_2 is calculated incorrectly, but that incorrect value is used correctly, the third point is earned. The fourth point is earned for using the values of H and C to get the mass of oxygen by difference. If one (or both) of the previously determined values is incorrect, but the student uses those incorrect values correctly, the fourth point is still earned.

(c) moles $\text{OH}^- = (0.08843 \text{ L})(0.102 \text{ mol/L}) = 0.00902 \text{ mol OH}^-$, *1 point*

therefore, 0.00902 mol H^+ neutralized, therefore $0.00902 \text{ mole acid}$

molar mass = $\frac{1.625 \text{ g}}{0.00902 \text{ mol}} = 180. \text{ g/mol}$ *1 point*

Note: The first point is earned for setting up the calculation to determine the number of moles of OH^- used in the titration; the second point is earned for using the number of moles of OH^- correctly to get the molar mass. If the number of moles of OH^- is incorrectly calculated, credit can be earned for this step if the student uses the incorrect value correctly.

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Question 3 (cont.)

- (d) (i) The pK_a is equal to the pH halfway to the equivalence point. ***1 point***

At 10.00 mL of added NaOH, pH = 3.44, therefore $pK_a = 3.44$

$$K_a = 10^{-3.44} = 3.6 \times 10^{-4}$$

- Other paths to the correct answer include using the initial data point and the acid equilibrium value, or using the Henderson-Hasselbalch equation

- (ii) Beyond the end point, there is excess OH^- , and the $[\text{OH}^-]$ determines the pH. ***1 point***

Moles of excess $\text{OH}^- = (0.00500 \text{ L})(0.100 \text{ mol/L}) = 5.00 \times 10^{-4} \text{ mol OH}^-$

$$[\text{OH}^-] = \frac{5.00 \times 10^{-4} \text{ mol OH}^-}{0.04000 \text{ L}} = 1.25 \times 10^{-2} \text{ M OH}^-$$

$$\text{pOH} = 1.90$$

$$\text{pH} = \mathbf{12.10}$$

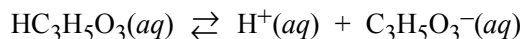
1 point

Note: The first point is earned for recognizing that the pH past the end point is determined by the amount of excess OH^- ions; the second point is earned for the calculations and the final answer.

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Question 1

10 points



1. Lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M $\text{HC}_3\text{H}_5\text{O}_3(aq)$ at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.

(a) Write the expression for the acid-dissociation constant, K_a , for lactic acid and calculate its value.

$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$ $0.50 \text{ M} \times 0.0166 = 0.0083 \text{ M} = x$ $\text{HC}_3\text{H}_5\text{O}_3(aq) \rightarrow \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)$ <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 10px;">0.50</td> <td style="padding-right: 10px;">~0</td> <td>0</td> </tr> <tr> <td>C</td> <td>-x</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.50 - x</td> <td>+x</td> <td>+x</td> </tr> </table> $K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{[0.0083][0.0083]}{[0.50 - 0.0083]}$ $K_a = 1.4 \times 10^{-4}$	I	0.50	~0	0	C	-x	+x	+x	E	0.50 - x	+x	+x	<p>1 point earned for equilibrium expression</p> <p>1 point earned for amount of $\text{HC}_3\text{H}_5\text{O}_3$ dissociating</p> <p>1 point earned for $[\text{H}^+] = [\text{C}_3\text{H}_5\text{O}_3^-]$ set up and solution</p>
I	0.50	~0	0										
C	-x	+x	+x										
E	0.50 - x	+x	+x										

(b) Calculate the pH of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$.

<p>From part (a):</p> $[\text{H}^+] = 0.0083 \text{ M}$ $\text{pH} = -\log [\text{H}^+] = -\log (0.0083) = 2.08$	<p>1 point earned for correctly calculating pH</p>
--	--

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Question 1 (cont'd.)

- (c) Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, $\text{NaC}_3\text{H}_5\text{O}_3$, in 250. mL of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$. Assume that volume change is negligible.

$\frac{0.045 \text{ mol NaC}_3\text{H}_5\text{O}_3}{0.250 \text{ L}} = 0.18 \text{ M C}_3\text{H}_5\text{O}_3^-$ $\text{HC}_3\text{H}_5\text{O}_3(aq) \rightarrow \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)$ <table style="margin-left: 20px;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 20px;">0.50</td> <td style="padding-right: 20px;">~0</td> <td>0.18</td> </tr> <tr> <td>C</td> <td>-x</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.50 - x</td> <td>+x</td> <td>0.18 + x</td> </tr> </table> $K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{[x][0.18 + x]}{[0.50 - x]}$ <p>Assume that $x \ll 0.18 \text{ M}$</p> $K_a = 1.4 \times 10^{-4} = \frac{[x][0.18]}{[0.50]}$ $x = 3.9 \times 10^{-4} \text{ M} = [\text{H}^+]$ $\text{pH} = -\log [\text{H}^+] = -\log (3.9 \times 10^{-4}) = 3.41$ <p>OR</p> $\text{pH} = \text{p}K_a + \log \frac{0.18 \text{ or } 0.045}{0.50 \quad 0.125} = 3.41$	I	0.50	~0	0.18	C	-x	+x	+x	E	0.50 - x	+x	0.18 + x	<p>1 point earned for $[\text{C}_3\text{H}_5\text{O}_3^-]$ (or $0.250 \text{ L} \times 0.50 \text{ mol/L} = 0.125$ mol $\text{HC}_3\text{H}_5\text{O}_3$ and 0.045 mol $\text{C}_3\text{H}_5\text{O}_3^-$)</p> <p>1 point earned for $[\text{H}^+]$ (set up and calculation)</p> <p>1 point earned for calculating the value of pH</p>
I	0.50	~0	0.18										
C	-x	+x	+x										
E	0.50 - x	+x	0.18 + x										

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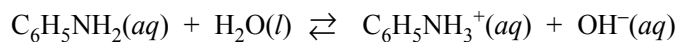
Question 1 (cont'd.)

- (d) A 100. mL sample of 0.10 *M* HCl is added to 100. mL of 0.50 *M* HC₃H₅O₃. Calculate the molar concentration of lactate ion, C₃H₅O₃⁻, in the resulting solution.

$0.50 \text{ M HC}_3\text{H}_5\text{O}_3 \left(\frac{100 \text{ mL}}{200 \text{ mL}} \right) = 0.25 \text{ M HC}_3\text{H}_5\text{O}_3$ $0.10 \text{ M HCl} \left(\frac{100 \text{ mL}}{200 \text{ mL}} \right) = 0.050 \text{ M H}^+$ $\text{HC}_3\text{H}_5\text{O}_3(aq) \rightarrow \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)$ <table style="margin-left: 40px;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 20px;">0.25</td> <td style="padding-right: 20px;">0.050</td> <td>0</td> </tr> <tr> <td>C</td> <td>-x</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.25 - x</td> <td>0.050 + x</td> <td>+x</td> </tr> </table> $K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{[0.050 + x][x]}{[0.25 - x]}$ <p>Assume $x \ll 0.050 \text{ M}$</p> $K_a = 1.4 \times 10^{-4} = \frac{[0.050][x]}{[0.25]}$ $x = 7.0 \times 10^{-4} \text{ M} = [\text{C}_3\text{H}_5\text{O}_3^-]$	I	0.25	0.050	0	C	-x	+x	+x	E	0.25 - x	0.050 + x	+x	<p>1 point earned for initial [H⁺] and [HC₃H₅O₃]</p> <p>OR</p> <p>(10 mmol H⁺; 50 mmol HC₃H₅O₃)</p> <p>1 point earned for showing dilution or moles of each</p> <p>1 point earned for [C₃H₅O₃⁻] setup and calculation</p>
I	0.25	0.050	0										
C	-x	+x	+x										
E	0.25 - x	0.050 + x	+x										

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Question 1



1. Aniline, a weak base, reacts with water according to the reaction represented above.

(a) Write the equilibrium expression, K_b , for the reaction represented above.

$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$	1 point for correct expression
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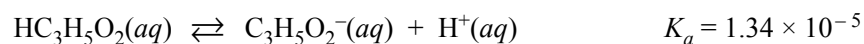
(b) A sample of aniline is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant, K_b , for this reaction.

<p>pH = 8.82</p> <p>pOH = 14 – 8.82 = 5.18</p> <p>$[\text{OH}^-] = 10^{-5.18} = 6.61 \times 10^{-6} \text{ M}$</p> <p>$[\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{OH}^-] = 6.6 \times 10^{-6} \text{ M}$</p> <p>$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(6.6 \times 10^{-6})^2}{0.10}$</p> <p>$K_b = 4.4 \times 10^{-10}$</p>	<p style="text-align: center;">1 point for calculation of $[\text{OH}^-]$</p> <p style="text-align: center;">1 point for $[\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{OH}^-]$</p> <p style="text-align: center;">1 point for calculation of K_b</p>
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Note: Following this point, any value of K_b obtained must be carried through.

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Question 1



Propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$, ionizes in water according to the equation above.

(a) Write the equilibrium-constant expression for the reaction.

$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]}$ <p><u>Notes:</u> Correct expression without K_a earns 1 point. Entering the value of K_a is acceptable. Charges must be correct to earn 1 point.</p>	<p>One point is earned for the correct equilibrium expression.</p>
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(b) Calculate the pH of a 0.265 M solution of propanoic acid.

$\text{HC}_3\text{H}_5\text{O}_2(aq) \rightleftharpoons \text{C}_3\text{H}_5\text{O}_2^-(aq) + \text{H}^+(aq)$ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px 10px;">I</td> <td style="padding: 2px 10px;">0.265</td> <td style="padding: 2px 10px;">0</td> <td style="padding: 2px 10px;">~0</td> </tr> <tr> <td style="padding: 2px 10px;">C</td> <td style="padding: 2px 10px;">-x</td> <td style="padding: 2px 10px;">+x</td> <td style="padding: 2px 10px;">+x</td> </tr> <tr> <td style="padding: 2px 10px;">E</td> <td style="padding: 2px 10px;">0.265 - x</td> <td style="padding: 2px 10px;">+x</td> <td style="padding: 2px 10px;">+x</td> </tr> </table> $K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(x)}{(0.265 - x)}$ <p>Assume that $0.265 - x \approx 0.265$,</p> <p>then $1.34 \times 10^{-5} = \frac{x^2}{0.265}$</p> $(1.34 \times 10^{-5})(0.265) = x^2$ $3.55 \times 10^{-6} = x^2$ $x = [\text{H}^+] = 1.88 \times 10^{-3} M$ $\text{pH} = -\log [\text{H}^+] = -\log (1.88 \times 10^{-3})$ $\text{pH} = 2.725$	I	0.265	0	~0	C	-x	+x	+x	E	0.265 - x	+x	+x	<p>One point is earned for recognizing that $[\text{H}^+]$ and $[\text{C}_3\text{H}_5\text{O}_2^-]$ have the same value in the equilibrium expression.</p> <p>One point is earned for calculating $[\text{H}^+]$.</p> <p>One point is earned for calculating the correct pH.</p>
I	0.265	0	~0										
C	-x	+x	+x										
E	0.265 - x	+x	+x										

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Question 1 (continued)

(c) A 0.496 g sample of sodium propanoate, $\text{NaC}_3\text{H}_5\text{O}_2$, is added to a 50.0 mL sample of a 0.265 M solution of propanoic acid. Assuming that no change in the volume of the solution occurs, calculate each of the following.

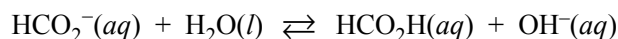
(i) The concentration of the propanoate ion, $\text{C}_3\text{H}_5\text{O}_2^-(aq)$ in the solution

$\text{mol NaC}_3\text{H}_5\text{O}_2 = 0.496 \text{ g NaC}_3\text{H}_5\text{O}_2 \times \frac{1 \text{ mol NaC}_3\text{H}_5\text{O}_2}{96.0 \text{ g NaC}_3\text{H}_5\text{O}_2}$ $\text{mol NaC}_3\text{H}_5\text{O}_2 = 5.17 \times 10^{-3} \text{ mol NaC}_3\text{H}_5\text{O}_2 = \text{mol C}_3\text{H}_5\text{O}_2^-$ $[\text{C}_3\text{H}_5\text{O}_2^-] = \frac{\text{mol C}_3\text{H}_5\text{O}_2^-}{\text{volume of solution}} = \frac{5.17 \times 10^{-3} \text{ mol C}_3\text{H}_5\text{O}_2^-}{0.050 \text{ L}} = 0.103 \text{ M}$	<p>One point is earned for calculating the number of moles of $\text{NaC}_3\text{H}_5\text{O}_2$.</p> <p>One point is earned for the molarity of the solution.</p>
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(ii) The concentration of the $\text{H}^+(aq)$ ion in the solution

$\text{HC}_3\text{H}_5\text{O}_2(aq) \rightleftharpoons \text{C}_3\text{H}_5\text{O}_2^-(aq) + \text{H}^+(aq)$ <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 10px;">0.265</td> <td style="padding-right: 10px;">0.103</td> <td style="padding-right: 10px;">~0</td> </tr> <tr> <td>C</td> <td>-x</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.265 - x</td> <td>0.103 + x</td> <td>+x</td> </tr> </table> $K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(0.103 + x)}{(0.265 - x)}$ <p>Assume that $0.103 + x \approx 0.103$ and $0.265 - x \approx 0.265$</p> $K_a = 1.34 \times 10^{-5} = \frac{(x)(0.103)}{0.265}$ $x = [\text{H}^+] = (1.34 \times 10^{-5}) \times \frac{0.265}{0.103} = 3.45 \times 10^{-5} \text{ M}$	I	0.265	0.103	~0	C	-x	+x	+x	E	0.265 - x	0.103 + x	+x	<p>One point is earned for calculating the value of $[\text{H}^+]$.</p>
I	0.265	0.103	~0										
C	-x	+x	+x										
E	0.265 - x	0.103 + x	+x										

The methanoate ion, $\text{HCO}_2^-(aq)$, reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.



(d) Given that $[\text{OH}^-]$ is $4.18 \times 10^{-6} \text{ M}$ in a 0.309 M solution of sodium methanoate, calculate each of the following.

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Question 1 (continued)

(i) The value of K_b for the methanoate ion, $\text{HCO}_2^-(aq)$

$\text{HCO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_2\text{H} + \text{OH}^-(aq)$ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 10px;">0.309</td> <td style="padding-right: 10px;">-</td> <td style="padding-right: 10px;">0</td> <td style="padding-right: 10px;">~0</td> </tr> <tr> <td>C</td> <td>-x</td> <td>-</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.309 - x</td> <td>-</td> <td>+x</td> <td>+x</td> </tr> </table> <p>$x = [\text{OH}^-] = 4.18 \times 10^{-6} M$</p> $K_b = \frac{[\text{OH}^-][\text{HCO}_2\text{H}]}{[\text{HCO}_2^-]} = \frac{(x)(x)}{(0.309 - x)} = \frac{(4.18 \times 10^{-6})^2}{(0.309 - x)}$ <p>x is very small ($4.18 \times 10^{-6} M$), therefore $0.309 - x \approx 0.309$</p> $K_b = \frac{(4.18 \times 10^{-6})^2}{0.309} = 5.65 \times 10^{-11}$	I	0.309	-	0	~0	C	-x	-	+x	+x	E	0.309 - x	-	+x	+x	<p>One point is earned for substituting 4.18×10^{-6} for both $[\text{OH}^-]$ and $[\text{HCO}_2\text{H}]$, and for calculating the value of K_b.</p>
I	0.309	-	0	~0												
C	-x	-	+x	+x												
E	0.309 - x	-	+x	+x												

(ii) The value of K_a for methanoic acid, HCO_2H

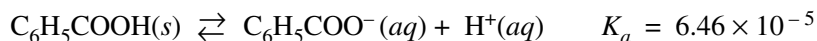
$K_w = K_a \times K_b$ $K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{5.65 \times 10^{-11}}$ $K_a = 1.77 \times 10^{-4}$	<p>One point is earned for calculating a value of K_a from the value of K_b determined in part (d)(i).</p>
--	--

(e) Which acid is stronger, propanoic acid or methanoic acid? Justify your answer.

<p>K_a for propanoic acid is 1.34×10^{-5}, and K_a for methanoic acid is 1.77×10^{-4}. For acids, the larger the value of K_a, the greater the strength; therefore methanoic acid is the stronger acid because $1.77 \times 10^{-4} > 1.34 \times 10^{-5}$.</p>	<p>One point is earned for the correct choice and explanation based on the K_a calculated for methanoic acid in part (d)(ii).</p>
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Question 1



1. Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 M NaOH.

(a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.

(i) $[\text{H}^+]$ in the solution

$[\text{H}^+] = 10^{-4.37} M = 4.3 \times 10^{-5} M$	One point is earned for the correct answer.
--	---

(ii) $[\text{OH}^-]$ in the solution

$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14} M^2}{4.3 \times 10^{-5} M} = 2.3 \times 10^{-10} M$	One point is earned for the correct answer.
---	---

(iii) The number of moles of NaOH added

$\text{mol OH}^- = 0.0150 \text{ L} \times 0.150 \text{ mol L}^{-1} = 2.25 \times 10^{-3} \text{ mol}$	One point is earned for the correct answer.
--	---

(iv) The number of moles of $\text{C}_6\text{H}_5\text{COO}^-(aq)$ in the solution

$\text{mol OH}^- \text{ added} = \text{mol C}_6\text{H}_5\text{COO}^-(aq) \text{ generated, thus}$ $\text{mol C}_6\text{H}_5\text{COO}^-(aq) \text{ in solution} = 2.25 \times 10^{-3} \text{ mol}$	One point is earned for the correct answer.
--	---

(v) The number of moles of $\text{C}_6\text{H}_5\text{COOH}$ in the solution

$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \Rightarrow [\text{C}_6\text{H}_5\text{COOH}] = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{K_a}$ $[\text{C}_6\text{H}_5\text{COOH}] = \frac{(4.3 \times 10^{-5} M) \times \frac{2.25 \times 10^{-3} \text{ mol}}{0.040 \text{ L}}}{6.46 \times 10^{-5}} = 3.7 \times 10^{-2} M$ <p>thus, $\text{mol C}_6\text{H}_5\text{COOH} = (0.040 \text{ L})(3.7 \times 10^{-2} M) = 1.5 \times 10^{-3} \text{ mol}$</p>	<p>One point is earned for the correct molarity.</p> <p>One point is earned for the correct answer.</p>
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Question 1 (continued)

Alternative solution for part (a)(v):

$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$ $\Rightarrow \text{pH} - \text{p}K_a = \log [\text{C}_6\text{H}_5\text{COO}^-] - \log [\text{C}_6\text{H}_5\text{COOH}]$ $\Rightarrow \log [\text{C}_6\text{H}_5\text{COOH}] = \log [\text{C}_6\text{H}_5\text{COO}^-] - (\text{pH} - \text{p}K_a)$ $= \log \left(\frac{2.25 \times 10^{-3} \text{ mol}}{0.040 \text{ L}} \right) - (4.37 - 4.190)$ $= -1.25 - 0.18 = -1.43$ $\Rightarrow [\text{C}_6\text{H}_5\text{COOH}] = 10^{-1.43} = 3.7 \times 10^{-2} M$ <p>thus, mol $\text{C}_6\text{H}_5\text{COOH} = (0.040 \text{ L})(3.7 \times 10^{-2} M) = 1.5 \times 10^{-3} \text{ mol}$</p>	
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(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

<p>At the equivalence point the solution is <u>basic</u> due to the presence of $\text{C}_6\text{H}_5\text{COO}^-$ (the conjugate base of the weak acid) that hydrolyzes to produce a basic solution as represented below.</p> $\text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COOH} + \text{OH}^-$	<p>One point is earned for the prediction <u>and</u> the explanation.</p>
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In a different titration, a 0.7529 g sample of a mixture of solid $\text{C}_6\text{H}_5\text{COOH}$ and solid NaCl is dissolved in water and titrated with 0.150 M NaOH . The equivalence point is reached when 24.78 mL of the base solution is added.

(c) Calculate each of the following.

(i) The mass, in grams, of benzoic acid in the solid sample

$\text{mol } \text{C}_6\text{H}_5\text{COOH} = (0.02478 \text{ L}) \times (0.150 \text{ mol OH}^- \text{ L}^{-1}) \times \frac{1 \text{ mol } \text{C}_6\text{H}_5\text{COOH}}{1 \text{ mol OH}^-}$ $= 3.72 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH}$ $\text{mass } \text{C}_6\text{H}_5\text{COOH} = 3.72 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH} \times \frac{122 \text{ g } \text{C}_6\text{H}_5\text{COOH}}{1 \text{ mol } \text{C}_6\text{H}_5\text{COOH}}$ $= 0.453 \text{ g } \text{C}_6\text{H}_5\text{COOH}$	<p>One point is earned for the correct answer.</p>
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Question 1 (continued)

(ii) The mass percentage of benzoic acid in the solid sample

$\begin{aligned} \text{mass \% C}_6\text{H}_5\text{COOH} &= \frac{0.453 \text{ g C}_6\text{H}_5\text{COOH}}{0.7529 \text{ g}} \times 100 \\ &= 60.2\% \end{aligned}$	<p style="text-align: center;">One point is earned for the correct answer.</p>
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