AP® CHEMISTRY
2014 SCORING GUIDELINES

Question 2
(10 points)

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

CH_3CH_2COOH and $CH_3CH_2COO^-$ *acid* *base* OR H_3O^+ and H_2O *acid* *base*	1 point is earned for writing (or naming) either of the Brønsted-Lowry conjugate acid-base pairs with a clear indication of which is the acid and which is the base.

(b) Determine the value of K_a for propanoic acid at 25°C.

$[H_3O^+] = 10^{-pH} = 10^{-2.79} = 1.6 \times 10^{-3}\ M$ $[CH_3CH_2COO^-] = [H_3O^+]$ AND $[CH_3CH_2COOH] = 0.20\ M - [H_3O^+]$, OR $[CH_3CH_2COOH] \approx 0.20\ M$ (state or assume that $[H_3O^+] << 0.20\ M$) $K_a = \frac{[CH_3CH_2COO^-][H_3O^+]}{[CH_3CH_2COOH]} = \frac{\left(1.6 \times 10^{-3}\ M\right)^2}{0.20\ M} = 1.3 \times 10^{-5}$	1 point is earned for correctly solving for $[H_3O^+]$. 1 point is earned for the K_a expression for propanoic acid OR 1 point is earned for substituting values into the K_a expression. 1 point is earned for correctly solving for the value of K_a.

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00.

False. The conjugate base of a weak acid undergoes hydrolysis (see equation below) at equivalence to form a solution with a pH > 7. $\left(CH_3CH_2COO^- + H_2O \rightleftarrows CH_3CH_2COOH + OH^-\right)$	1 point is earned for noting that the statement is false AND providing a supporting explanation.

Question 2 (continued)

(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

True. HCl is a strong acid that ionizes completely. Fewer moles of HCl are needed to produce the same $[H_3O^+]$ as the propanoic acid solution, which only partially ionizes.	1 point is earned for noting that the statement is true and providing a supporting explanation.

A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 *M* NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 *M* NaOH, reaching the end point after 20.52 mL of the base solution has been added.

(d) Calculate the molarity of the propanoic acid solution.

Let x = moles of propanoic acid then $x = (0.02052 \text{ L NaOH}) \times \frac{0.173 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol acid}}{1 \text{ mol NaOH}}$ $= 3.55 \times 10^{-3}$ mol propanoic acid $\frac{3.55 \times 10^{-3} \text{ mol acid}}{0.02500 \text{ L acid}} = 0.142 \ M$ OR Since CH_3CH_2COOH is monoprotic and, at the equivalence point, moles H^+ = moles OH^-, then $M_A V_A = M_B V_B$ $M_A = \frac{M_B V_B}{V_A} = \frac{(0.173 \ M \text{ NaOH})(20.52 \text{ mL NaOH})}{25.00 \text{ mL acid}} = 0.142 \ M$	1 point is earned for correctly calculating the number of moles of acid that reacted at the equivalence point. 1 point is earned for the correct molarity of acid.

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

Question 2 (continued)

Disagree with the student's claim From part (b) above, pK_a for propanoic acid is $\log(1.3 \times 10^{-5}) = 4.89$. Because 4.83 is so close to 4.89, the pH at the equivalence point in the titration of butanoic acid should be close enough to the pH in the titration of propanoic acid to make the original indicator appropriate for the titration of butanoic acid.	1 point is earned for disagreeing with the student's claim and making a valid justification using pK_a, K_a, or pH arguments. 1 point is earned for numerically comparing either: the two pK_a values, the two K_a values, or the two pH values at the equivalence point.

2A,

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

2. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

(b) Determine the value of K_a for propanoic acid at 25°C.

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00.

(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 *M* NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 *M* NaOH, reaching the end point after 20.52 mL of the base solution has been added.

(d) Calculate the molarity of the propanoic acid solution.

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

(2) a. Acid - CH_3CH_2COOH

Conjugate base - $CH_3CH_2COO^-$

b. pH = 2.79 $[H_3O^+] = 10^{-2.79} = 0.0016\ M\ H_3O^+$

$CH_3CH_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2COO^-$

I:	0.20 M		
C:	−0.0016 M	+0.0016 M	+0.0016 M
E:	0.20 M	0.0016 M	0.0016 M

$$K_a = \frac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

$$= \frac{(0.0016)(0.0016)}{0.20}$$

$$= 1.3 \times 10^{-5}$$

$K_a = 1.3 \times 10^{-5}$

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c. (i) False. When the CH_3CH_2COOH and NaOH react (with the specified molarity and volume), it will reach the equivalence point. However, due to the neutralization reaction, $CH_3CH_2COO^-$ increases in concentration, which is a relatively strong conjugate base. The base will cause the pH at the equivalence point to be higher than 7.00 because it ~~dissociates~~ reacts to increase the concentration of OH^-. ($K_b = \frac{1.00 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$)

(ii) True. HCl completely dissociates because it is a strong acid. Thus, the molarity of HCl equals the molarity of H^+. For propanoic acid, however, it only dissociates to a small degree, as shown by it's small Ka value of 1.3×10^{-5}. For this reason, a higher concentration of propanoic acid would be required to yield the same concentration of H_3O^+ because it does not completely dissociate. The same concentrations of H_3O^+ for the more concentrated propanoic acid and the less concentrated HCl would give the same pH value. ($pH = -\log [H_3O^+]$)

d. $NaOH + CH_3CH_2COOH \longrightarrow Na^+ + CH_3CH_2COO^- + H_2O$

$$\frac{0.173 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{0.02052 \text{ L}}{1} \times \frac{1 \text{ mol } CH_3CH_2COOH}{1 \text{ mol NaOH}} \times \frac{1}{0.02500 \text{ L}}$$

$$= \boxed{0.142 \text{ M } CH_3CH_2COOH}$$

e. The Ka value derived for propanoic acid is 1.3×10^{-5}. The pKa value ($-\log(1.3 \times 10^{-5})$) is 4.89. As 4.89 and 4.83 are very close to one another, the indicator used can be the same. If the pKa values are very similar,

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approximately the same concentration of H^+ will be in solution. The same amount (approximately) of OH^- will react and the two equivalence points will be extremely close. As indicators have pH ranges, using the same indicator for a slightly different acid should not make any significant difference.

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2B,

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

2. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base. ✓

(b) Determine the value of K_a for propanoic acid at 25°C. ✓

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00. ✓

(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution. ✓

A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 *M* NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 *M* NaOH, reaching the end point after 20.52 mL of the base solution has been added.

(d) Calculate the molarity of the propanoic acid solution. ✓

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer. ✓

a) Acid → CH_3CH_2COOH

Base → $CH_3CH_2COO^-$

b) ~~pH / pKa / Hydrochloric acid~~ HCl

$10^{-2.79} = [H^+]$

$[H^+] = .0016$

$CH_3CH_2COOH + H_2O \rightleftarrows CH_3CH_2COO^- + H^+$			
.2M	—	0	0
.0016	—	+.0016	+.0016
.2−x	—	.0016	.0016

$K_a = x^2/.2-x$

$K_a = (.0016)^2/(.2-.0016)$

$K_a = 1.3 \times 10^{-5}$

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c i) False, after the propanoic acid reacts with the NaOH, they will produce CH_3CH_2COONa. while the acid and base will both be neutralized, the salt they formes will dissociate, and the $CH_3CH_2COO^-$ will hydrolyze, giving a basic pH.

$CH_3CH_2COOH + NaOH \rightarrow CH_3COONa + H_2O$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

ii) True, HCl is a stronger acid than propanoic acid. So if their pH is the same, the propanoic acid must be much more highly concentrated than the HCl.

d) $CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$

.173 M = x / .02052 L

x = .0035 mols NaOH added

1:1 ratio

.0035 mols propanoic acid

x = .0035 mol / .02052 L

x = .173 M

$pKa = \frac{[H_3O][CH_3CH_2COONa]}{[CH_3CH_2COOH][NaOH]}$

$1.3 \times 10^{-5} = \frac{(.173)}{(x)(.173)}$

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

$[CH_3CH_2COOH] = 1.3 \times 10^{-5}$

e) NO, the pKa of propanoic acid is about 4.89. Because of the similarities of the 2 pKa's, it wont be neuessary to use a different indicator.

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2C1

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

2. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

$50.0\,mL\left(\frac{1L}{1000mL}\right) = 0.05\,L$

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

(b) Determine the value of K_a for propanoic acid at 25°C.

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00.

(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

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(d) Calculate the molarity of the propanoic acid solution.

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

a) Acid: CH_3CH_2COOH Base: $CH_3CH_2COO^-$

b) $K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$ $10^{-2.79} = 1.6\times10^{-3}\,M = [H^+]$ $K_a = \frac{x^2}{0.2}$

$[CH_3CH_2COOH] = 0.2\,M$

$K_a = \frac{(1.6\times10^{-3})(1.6\times10^{-3})}{0.2} = 1.28\times10^{-5}$

c) i) $pH = -\log(0.2) = 0.7$ true, because they are equal so their

$pOH = -\log(0.2) = 0.7$ pH becomes neutral (=7.00)

ii) M of $HCl = 10^{-2.79} = 0.002$ False because they are equal

M of $CH_3CH_2COOH = 10^{-2.79} = 0.002$

2C2

ADDITIONAL PAGE FOR ANSWERING QUESTION 2

d) $CH_3CH_2COOH + NaOH \rightarrow NaCH_3CH_2COO + H_2O$

$20.52\ mL \left(\frac{1\ L}{1000\ mL}\right) = 0.02052\ L\ NaOH$

$0.173\ M\ NaOH = \frac{x\ mol}{0.02052\ L}$ $\quad x\ mol = 0.00355\ mol\ NaOH$

$0.00355\ mol\ NaOH \left(\frac{1\ mol\ CH_3CH_2COOH}{1\ mol\ NaOH}\right) = 0.00355\ mol\ CH_3CH_2COOH$

$25.00\ mL \left(\frac{1\ L}{1000\ mL}\right) = 0.025\ L\ CH_3CH_2COOH$

$M\ CH_3CH_2COOH = \frac{0.00355\ mol}{0.025\ L} = 0.142$ $\boxed{0.14\ M\ CH_3CH_2COOH}$

e) yes because the two values are very different and from each other

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AP® CHEMISTRY
2014 SCORING COMMENTARY

Question 2

Overview

This question was designed to assess students' conceptual and analytical understanding of acid-base chemistry. Part (a) asked students to identify a Bronsted-Lowry conjugate acid-base pair from an equation provided. Part (b) asked students to calculate the K_a for propanoic acid given a pH and concentration. In part (c) students were provided with two statements and asked to identify each as true or false and support their answers with reasoning. In part (c)(i) the question assessed conceptual understanding of pH when equal volumes of equimolar strong base and weak acid solutions were mixed. In part (c)(ii) the question assessed conceptual understanding between concentration and pH of strong acid and weak acid solutions. Part (d) required students to calculate the molar concentration of propanoic acid given titration data. Part (e) assessed analytical and conceptual understanding of pK_a values and indicators.

Sample: 2A
Score: 10

This response earned all 10 possible points: 1 point in part (a), 3 points in part (b), 1 point in part (c)(i), 1 point in part (c)(ii), 2 points in part (d), and 2 points in part (e).

Sample: 2B
Score: 8

This response earned all the points except for the two points in part (d).

Sample: 2C
Score: 6

This response did not earn credit in either part (c)(i) or part (c)(ii) for incorrect conclusions and reasoning. In part (e) the response did not earn either of the two points. The student correctly calculates the value of K_a in part (b) but in part (e) the student incorrectly agrees with the statement that a new indicator is needed.