2. Propanoic acid, CH₃CH₂COOH, 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 CH₃CH₂COOH is 2.79.

(a) Identify a Bronsted-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 CH₃CH₂COOH 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.

\[
\text{HC}_9\text{H}_7\text{O}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_9\text{H}_7\text{O}_4^-(aq)
\]

7. The molecular formula of acetylsalicylic acid, also known as aspirin, is HC₉H₇O₄. The dissociation of HC₉H₇O₄(aq) is represented by the equation above. The pH of 0.0100 M HC₉H₇O₄(aq) is measured to be 2.78.

(a) Write the expression for the equilibrium constant, \( K_a \), for the reaction above.

(b) Calculate the value of \( K_a \) for acetylsalicylic acid.

(c) An aqueous solution of aspirin is buffered to have equal concentrations of HC₉H₇O₄(aq) and C₉H₇O₄⁻(aq). Calculate the pH of the solution.
75. A 0.10 M solution of which of the following salts is most basic?

(A) LiNO₃
(B) Na₂SO₄
(C) CaCl₂
(D) Al(NO₃)₃
(E) K₂CO₃

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^- \]

37. The acid-dissociation constants of HC₃H₅O₃(aq) and CH₃NH₃⁺(aq) are given in the table above. Which of the following mixtures is a buffer with a pH of approximately 3?

- A mixture of 100 mL of 0.1 M CH₃NH₃Cl and 50 mL of 0.1 M NaOH
- A mixture of 100 mL of 0.1 M HC₃H₅O₃ and 50 mL of 0.1 M NaOH
- A mixture of 100 mL of 0.1 M NaC₃H₅O₃ and 100 mL of 0.1 M NaOH

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

38. Data collected during the titration of a 20.0 mL sample of a 0.10 M solution of a monoprotic acid with a solution of NaOH of unknown concentration are plotted in the graph above. Based on the data, which of the following are the approximate pKₐ of the acid and the molar concentration of the NaOH?

<table>
<thead>
<tr>
<th>pKₐ</th>
<th>[NaOH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>4.7</td>
</tr>
<tr>
<td>(B)</td>
<td>4.7</td>
</tr>
<tr>
<td>(C)</td>
<td>9.3</td>
</tr>
<tr>
<td>(D)</td>
<td>9.3</td>
</tr>
</tbody>
</table>

10. An acetate buffer solution is prepared by combining 50 mL of 0.20 M acetic acid, HC₂H₃O₂(aq), and 50 mL of 0.20 M sodium acetate, NaC₂H₃O₂(aq). A 5.0 mL sample of 0.10 M NaOH(aq) is added to the buffer solution. Which of the following is a correct pairing of the acetate species present in greater concentration and of the pH of the solution after the NaOH(aq) is added? (The pKₐ of acetic acid is 4.7.)

<table>
<thead>
<tr>
<th>Acetate Species</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) HC₂H₃O₂</td>
<td>&lt; 4.7</td>
</tr>
<tr>
<td>(B) HC₂H₃O₂⁺</td>
<td>&gt; 4.7</td>
</tr>
<tr>
<td>(C) C₂H₃O₂⁻</td>
<td>&lt; 4.7</td>
</tr>
<tr>
<td>(D) C₂H₃O₂⁻</td>
<td>&gt; 4.7</td>
</tr>
</tbody>
</table>
Questions 14-17 refer to the following.

15. Which of the following is the best particulate representation of the species (other than H$_2$O) that are present in significant concentrations in the solution at point $U$ in the titration?

(A) [Diagram A]
(B) [Diagram B]
(C) [Diagram C]
(D) [Diagram D]
16. At which point on the titration curve is $[A^-]$ closest to twice that of $[HA]$?

- (A) $R$
- (B) $S$
- (C) $T$
- (D) $U$

17. A student carries out the same titration, but uses an indicator instead of a pH meter. If the indicator changes color slightly past the equivalence point, what will the student obtain for the calculated concentration of the acid?

- (A) Slightly less than 0.0800 $M$
- (B) Slightly more than 0.0800 $M$
- (C) Slightly less than 0.125 $M$
- (D) Slightly more than 0.125 $M$

29. On the basis of the information above, the dissolution of $\text{FeF}_2(s)$ in acidic solution is

- (A) thermodynamically favorable, because $K_2 > 1$
- (B) thermodynamically favorable, because $K_3 > 1$
- (C) not thermodynamically favorable, because $K_1 < 1$
- (D) not thermodynamically favorable, because $K_3 < 1$

15. A solution is prepared by mixing 50 mL of 1 $M$ $\text{NaH}_2\text{PO}_4$ with 50 mL of 1 $M$ $\text{Na}_2\text{HPO}_4$. On the basis of the information above, which of the following species is present in the solution at the lowest concentration?

- (A) $\text{Na}^+$
- (B) $\text{HPO}_4^{2-}$
- (C) $\text{H}_2\text{PO}_4^-$
- (D) $\text{PO}_4^{3-}$

48. Which of the following correctly ranks the three monoprotic acids listed in the table above from the weakest to the strongest?

- (A) $X < Y < Z$
- (B) $X < Z < Y$
- (C) $Y < Z < X$
- (D) $Z < Y < X$
PRACTICE QUESTION SOLUTIONS.

#2.

\[ \text{CH}_3\text{CH}_2\text{COOH}^{(aq)} + \text{H}_2\text{O}^{(l)} \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-\text{aq} + \text{H}_3\text{O}^+\text{aq} \]

\[ \text{pH} = 2.79 = -\log [\text{H}_3\text{O}^+] \]

\[ [\text{CH}_3\text{CH}_2\text{COOH}] = 0.20 \text{ M} \]

50.0 mL solution

(a) \text{CH}_3\text{CH}_2\text{COOH}^{+} - \text{acid} \\
\text{CH}_3\text{CH}_2\text{COO}^- - \text{conjugate base} \\
\text{H}_2\text{O} - \text{base} \\
\text{H}_3\text{O}^+ - \text{conjugate acid}

(b) \[ K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} \]

\[ [\text{H}_3\text{O}^+] = [\text{CH}_3\text{CH}_2\text{COO}^-] = 10^{-2.79} = 0.00162 \text{ M} \]

\[ K_a = \left(\frac{0.00162}{0.20}\right)^2 = \boxed{1.3 \times 10^{-5}} \]

(c) False. The pH will be greater than 7.00. NaOH is a strong base and \text{CH}_3\text{CH}_2\text{COOH} is a weak acid. At equilibrium, the equivalence point when equal moles of acid and base have reacted, the following hydrolysis
takes place:
\[ \text{CH}_3\text{CH}_2\text{COO}^- \cdot (aq) + \text{H}_2\text{O}(l) = \text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^- \cdot (aq) \]

The production of OH\(^-\) at equivalence causes a basic solution to form.

ii. True. For HCl, a strong acid, \([\text{H}_3\text{O}^+]\) is equal to \([\text{HCl}]\) since all HCl dissociates into \(\text{H}_3\text{O}^+\) and Cl\(^-\) in water. For a weak acid such as propanoic acid, the \([\text{H}_3\text{O}^+]\) is much less than the \([\text{CH}_3\text{CH}_2\text{COOH}]\) because a weak acid dissociates only slightly in water. In order for pH to be equivalent for solutions of these acids, the \([\text{H}_3\text{O}^+]\) must be equivalent; \(pH = -\log [\text{H}_3\text{O}^+]\). This can only be true if \([\text{CH}_3\text{CH}_2\text{COOH}] > [\text{HCl}]\).

(d) \([\text{NaOH}] = 0.173 \text{ M}\)

\[\text{volume CH}_3\text{CH}_2\text{COOH} = 25.00\text{mL} = 0.02500 \text{ L}\]

\[\text{volume NaOH} = 20.52 \text{ mL} = 0.02052 \text{ L}\]

\[\text{mole NaOH} = \text{mole CH}_3\text{CH}_2\text{COOH} = 0.173 \text{ mol} \times 0.02052 \text{ L}\]

\[\text{mole} = 0.00355 \text{ mol}\]

\[\frac{\text{mol}}{1 \text{ L}}\]

\[\text{[CH}_3\text{CH}_2\text{COOH}] = \frac{0.00355 \text{ mol}}{0.02500 \text{ L}} = 0.142 \text{ M}\]
#7

\[\text{H}_2\text{CaH}_2\text{O}_4^{(aq)} + \text{H}_2\text{O}^{(l)} \rightarrow \text{H}_3\text{O}^{+}(aq) + \text{CaH}_2\text{O}_4^{-}(aq)\]

\[\text{pH} = 2.78 = -\log [\text{H}_3\text{O}^{+}]\]

\[0.01\text{M} \quad \text{for } [\text{H}_2\text{CaH}_2\text{O}_4] = 0.01\text{ M}\]

(a) \[K_a = \frac{[\text{H}_3\text{O}^{+}][\text{CaH}_2\text{O}_4^{-}]}{[\text{H}_2\text{CaH}_2\text{O}_4]}\]

(b) \[\text{pH} = -\log [\text{H}_3\text{O}^{+}] = 2.78 = 1.66 \times 10^{-2} \text{ M}\]

\[K_a = \frac{(0.00166)^2}{0.01} = \frac{2.8 \times 10^{-4}}{0.01}\]

(c) If \([\text{H}_2\text{CaH}_2\text{O}_4] = [\text{CaH}_2\text{O}_4^{-}]\), then...

\[\log \frac{[\text{A}^{-}]}{[\text{HA}]} = \log \frac{[\text{CaH}_2\text{O}_4^{-}]}{[\text{H}_2\text{CaH}_2\text{O}_4]} = \log 1 = 0\]

and...

\[\text{pH} = \text{p}K_a + \log \frac{[\text{CaH}_2\text{O}_4^{-}]}{[\text{H}_2\text{CaH}_2\text{O}_4]} = \text{p}K_a + 0 = \text{p}K_a\]

\[\text{pH} = \text{p}K_a = -\log (2.8 \times 10^{-4}) = 3.56\]
MC Explanations.

35. A basic salt will contain the conjugate base of a weak acid. Thus ions produce OH⁻ when hydrolyzed.

- Li⁺, Na⁺, Ca²⁺ and K⁺ do not hydrolyze, since they are derived from strong bases.
- NO₃⁻, SO₄²⁻, Cl⁻ also do not hydrolyze, since they are derived from strong acids.

- Only Al³⁺ and CO₃²⁻ hydrolyze.

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 + 3\text{H}^+ \]
\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- \] basic

37. \( \text{pH} = \text{pK}_a + \log \left( \frac{[A^-]}{[HA]} \right) \). If \([A^-] = [HA]\), then \( \log 1 = 0 \) and \( \text{pH} = \text{pK}_a \). The approximate \( \text{pK}_a \) of \( \text{HC}_2\text{H}_3\text{O}_3 \) is between 3 and 4 and \( \text{CH}_3\text{NH}_3^+ \) is between 10 and 11. (Estimating from the exponents of \( \text{K}_a \)). So a solution that contains equal \([A^-]\) of \( \text{HC}_2\text{H}_3\text{O}_3 \) and \( \text{C}_3\text{H}_5\text{O}_3^- \) will be a buffer with a \( \text{pH} \) of about 3.

When \( \text{HC}_2\text{H}_3\text{O}_3 \) is mixed with \( \text{NaOH} \):

\[ \text{HC}_2\text{H}_3\text{O}_3 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{C}_3\text{H}_5\text{O}_3^- \]

\[ \begin{array}{c|c|c|c}
0.01 \text{ mol} & 0.005 \text{ mol} & - & 0 \\
-0.005 & -0.005 & +0.005 & \\
0.005 \text{ mol} & 0 & 0.005 \text{ mol} & \\
\end{array} \]

Equal amount of \([A^-]\) and \([HA]\).
pK<sub>a</sub> of the acid = pH at half-equivalence.
The volume of titrant at half equivalence is 10.0 mL and the pH here is around 5... eliminate (c) and (d).
A monoprotic acid, HA and NaOH have the following neutralization...

\[ HA + NaOH \rightarrow H_2O + NaA \]

Moles HA = M·L·NaOH

\[ \frac{(\text{Volume} \ HA)([HA])}{[NaOH]} = \frac{(\text{Volume} \ NaOH)([NaOH])}{[NaOH]} \]

\[ \frac{(20.0 \ mL)(0.10 \ M)}{[NaOH]} = \frac{20.0 \ mL}{[NaOH]} \]

\[ [NaOH] = 0.10 \ M. \]

\[ \text{add} \ 0.005 \ L \times 0.10 \ M \ NaOH = 0.0005 \ mL \ OH^- \]

10. \[ HC_2H_3O_2 + H_2O \rightarrow C_2H_3O_2^- + H_3O^+ \]

\[ 0.01 = 0.01 \]

\[ -0.0005 = +0.0005 \]

\[ 0.0005 \text{ mol} \rightarrow 0.0005 \text{ mol} \]

\[ \text{more } C_2H_3O_2^- \text{ present} \]

pH will be greater than 4.7 because there is a higher [ ] of basic species, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>\textsuperscript{-} in the solution.
14. Equivalence occurs at 40.0 mL titrant added so 1/2 equivalence @ 20.0 mL of titrant.
   At 1/2 eq., [HA] = [A^-]. Below 1/2 eq., more acid species present, i.e. HA.

15. At U, there is an excess of OH^-, causing a basic pH. Na^+ and A^- are spectators.

16. Above the 1/2 eq. point, there is more conj. base A^- than HA. At U, [A^-] = [HA],
    at "R", [A^-] < [HA] and at "T", [A^-] > [HA].

17. [NaOH] = 0.100 M
    volume NaOH • 40.0 mL @ Eq.
    volume HA = 50.0 mL
    moles NaOH = mols HA = 0.100 M • 0.0400 L = 0.00400 mol

    [HA] = \frac{0.00400 \text{ mol}}{0.0500 \text{ L}} = 0.08 \text{ M}

    Going past the eq. point will mean that volume of NaOH is greater than 40.0 mL. The number of
    moles of NaOH and HA calculated will be greater than 0.00400 mol and [HA] will be over 0.08 M.
29. \[ K_1 = \frac{[F^-]^2 \cdot [Fe^{2+}]}{[FeF_2]} = 2 \times 10^{-6} \]

\[ K_2 = \frac{[HF]}{[F^-] \cdot [H^+]} = 1 \times 10^7 \]

\[ K_3 = \frac{[Fe^{2+}] \cdot [HF]^2}{[FeF_2] \cdot [H^+]^2} \quad ? \]

\[ \frac{[HF]^2}{[F^-] \cdot [H^+]^2} = (1 \times 10^7)^2 \]

\[ \frac{[F^-]^2 \cdot [Fe^{2+}]}{[HF]^2} = 1 \times 10^6 \]

\[ \frac{[Fe^{2+}] \cdot [HF]^2}{[FeF_2] \cdot [H^+]^2} = \frac{(2 \times 10^{-6})}{(1 \times 10^6)} \]

\[ = 2 \times 10^{1} = 2 \]

15. \( K_a_3 \) is the smallest eq. constant \((10^{-19})\), so the products of that run will be present in the smallest concentration.

48. The \([X] \) is much less than \([Y] \) or \([Z] \) but the pH is nearly the same. It is the most dissociative of \( n = 3 \) if its \([H_3O^+] \) is nearly equal to the others. \( Z \) is the weakest acid since it has a greater \([X] \) than \( Y \) but only
48. X is the strongest acid. It has the lowest pH (most $[\text{H}_3\text{O}^+]$) and the lowest concentration. Eliminate (A) and (B). Both Y and Z have the same pH (same $[\text{H}_3\text{O}^+]$) but Z has a larger concentration. That means it must take more Z to dissociate into $8 \text{H}_3\text{O}^+$ as compared to Y. Z is the weakest acid.