Inside:

- Free Response Question 1
  - Scoring Guideline
  - Student Samples
  - Scoring Commentary
Question 1: Long Answer 10 points

(a) For the correct expression: 1 point

\[ K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} \]

(b) For the correct calculated concentration of H$_3$O$^+$: 1 point

\[
\begin{align*}
HCOOH + H_2O & \rightleftharpoons H_3O^+ + HCOO^- \\
I & \quad 0.25 \\
C & \quad -x \\
E & \quad 0.25 - x
\end{align*}
\]

\[
\begin{align*}
C & \quad +x \\
E & \quad x \\
\end{align*}
\]

Let \([H_3O^+] = x\), then

\[
1.8 \times 10^{-4} = \frac{x^2}{(0.25 - x)}
\]

Assume \(x << 0.25\), then

\[
1.8 \times 10^{-4} = \frac{x^2}{0.25} \Rightarrow x = 0.0067 \text{ M}
\]

For the correct calculated value of pH: 1 point

\[
pH = -\log[H_3O^+] = -\log(0.0067) = 2.17
\]

Total for part (b) 2 points

(c) For the correct diagram: 1 point

![Diagram](image)

(d) (i) For the correct balanced equation (state symbols not required): 1 point

\[ H_2NNH_3(aq) + HCOOH(aq) \rightarrow H_2NNH_3^+(aq) + HCOO^-(aq) \]

(ii) For the correct answer and a valid justification: 1 point

Acidic. The \(K_a\) of \(H_2NNH_3^+\) is greater than the \(K_b\) of \(HCOO^-\), so the production of \(H_3O^+\) \(\text{(aq)}\) occurs to a greater extent than the production of \(OH^-\) \(\text{(aq)}\).

Total for part (d) 2 points

(e) For the correct answer and a valid justification: 1 point

Accept one of the following:

- Yes. The oxidation number of hydrogen changes from +1 in HCOOH to zero in \(H_2\).
- Yes. The oxidation number of carbon changes from +2 in HCOOH to +4 in CO$_2$.

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### AP® Chemistry 2021 Scoring Guidelines

<table>
<thead>
<tr>
<th>(f)</th>
<th>For the correct calculated value of the pressure of CO₂ (may be implicit):</th>
<th>1 point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 atm total ( \times ) 1 atm CO₂ / 2 atm of product = 12 atm CO₂</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(f)</th>
<th>For the correct calculated number of moles of CO₂:</th>
<th>1 point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( PV = nRT )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = \frac{PV}{RT} = \frac{(12 \text{ atm})(4.3 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.1 \text{ mol CO₂} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(f)</th>
<th>Total for part (f)</th>
<th>2 points</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>(g)</th>
<th>For the correct answer and a valid justification:</th>
<th>1 point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>It would remain the same. In a catalyzed reaction the net amount of catalyst is constant.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(g)</th>
<th>Total for question 1</th>
<th>10 points</th>
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</thead>
</table>

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Begin your response to QUESTION 1 on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

\[
\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \quad K_a = 1.8 \times 10^{-4}
\]

1. Methanoic acid, HCOOH, ionizes according to the equation above.

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

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

   (b) Calculate the pH of a 0.25 M solution of HCOOH.

   \[
   \begin{align*}
   \text{HCOOH} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCOO}^- \\
   \text{L} & = -x \\
   E & = \frac{0.25}{x} \\
   C & = \frac{0}{x} \\
   \text{pH} & = -\log([\text{H}_3\text{O}^+]) \\
   \text{pH} & = 2.17
   \end{align*}
   \]

   \[
   \begin{align*}
   K_a & = 1.8 \times 10^{-4} \\
   \frac{x^2}{0.25} & = \frac{0.25}{x} \\
   x & = 0.00671 \text{ M}
   \end{align*}
   \]

Unauthorized copying or reuse of this page is illegal.
(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.

:O: \
\|  
H - C - O - H

H₂NNH₂(aq) + H₂O(l) ⇌ H₂NNH₃⁺(aq) + OH⁻(aq) \[ K_b = 1.3 \times 10^{-6} \]

(d) In aqueous solution, the compound H₂NNH₂ reacts according to the equation above. A 50.0 mL sample of 0.25 M H₂NNH₂(aq) is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H₂NNH₂ is combined with HCOOH.

\[ \text{HCOOH} + \text{H}_2\text{NNH}_2 \rightarrow \text{COOH}^- + \text{H}_2\text{NNH}_3^+ \]

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

\[ K_b \text{ for COOH}^- = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11} \]

\[ K_a \text{ for } \text{H}_2\text{NNH}_3^+ = \frac{1 \times 10^{-14}}{1.3 \times 10^{-6}} = 7.7 \times 10^{-9} \]

The resulting solution will be acidic since the conjugate acid of H₂NNH₂ is a stronger base than the conjugate base of HCOOH. It has a larger K⁺ value, so there will be a higher [H⁺].
When a catalyst is added to a solution of HCOOH(aq), the reaction represented by the following equation occurs.

\[
\text{HCOOH}(aq) \rightarrow \text{H}_2(g) + \text{CO}_2(g)
\]

(e) Is the reaction a redox reaction? Justify your answer.

Yes, since the oxidation numbers of some elements change. H goes from 1+ to 0.

(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of \text{CO}_2(g) produced in the reaction. (Assume that the amount of \text{CO}_2(g) dissolved in the solution is negligible.)

\[
\begin{align*}
P_{\text{total}} &= P_{\text{H}_2} + P_{\text{CO}_2} \\
24 \text{ atm} &= 12 \text{ atm} + P_{\text{CO}_2} \\
\Rightarrow P_{\text{CO}_2} &= 12 \text{ atm} \\
(12)(4.3) &= n(0.08204)(25+273) \\
n &= 2.11 \text{ mol} \\
\text{CO}_2 &= 2.1 \text{ mol}
\end{align*}
\]

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

The amount of the catalyst remains the same because a catalyst is not consumed or produced by a reaction or it is consumed and produced in a 1:1 ratio so its amount stays constant.
Begin your response to QUESTION 1 on this page.

CHEMISTRY
SECTION II
Time—1 hour and 45 minutes
7 Questions

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**Directions**: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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\[
\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \quad K_a = 1.8 \times 10^{-4}
\]

1. Methanoic acid, HCOOH, ionizes according to the equation above.

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

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

   (b) Calculate the pH of a 0.25 \(M\) solution of HCOOH.

\[
[H^+] = 0.25
\]

\[
1.8 \times 10^{-4} = \frac{x^2}{0.25 - x}
\]

\[
[1.5 \times 10^{-5} = x
\]

\[
x = 0.0067
\]

\[
\text{pH} = 2.17
\]
(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.

\[ H_2\text{NNH}_2(aq) + H_2O(l) \rightleftharpoons H_2\text{NNH}_3^+(aq) + OH^- (aq) \quad K_b = 1.3 \times 10^{-6} \]

(d) In aqueous solution, the compound H$_2$NNH$_2$ reacts according to the equation above. A 50.0 mL sample of 0.25 M H$_2$NNH$_2$(aq) is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H$_2$NNH$_2$ is combined with HCOOH.

\[ H_2\text{NNH}_2(aq) + HCOOH(aq) \rightleftharpoons H_2\text{NNH}_3^+(aq) + COOH^-(aq) \]

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

The resulting solution is neutral due to the combination of weak acids and bases in equimolar amounts.
Continue your response to **QUESTION 1** on this page.

When a catalyst is added to a solution of HCOOH\(_{(aq)}\), the reaction represented by the following equation occurs.

\[ \text{HCOOH}(aq) \rightarrow \text{H}_2(g) + \text{CO}_2(g) \]

(e) Is the reaction a redox reaction? Justify your answer.

This is not a redox reaction, because hydrogens are simply separated.

The reaction does not contain substances that reduce or oxidize each other.

(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of CO\(_2\)(g) produced in the reaction. (Assume that the amount of CO\(_2\)(g) dissolved in the solution is negligible.)

\[
\frac{pV}{RT} = \frac{1}{54.3} \times 25 + 273 \times 0.08 \approx 0.25 \text{ atm} \]

\[
\frac{(4.3)(2.4)}{(298)(0.08)} = 4.2 \text{ moles} 
\]

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

The amount of catalyst will remain the same, because it will appear as a product in equal mole as it is consumed.
Begin your response to **QUESTION 1** on this page.

**CHEMISTRY**

**SECTION II**

**Time**—1 hour and 45 minutes

**7 Questions**

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\[
\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \quad K_a = 1.8 \times 10^{-4}
\]

1. Methanoic acid, HCOOH, ionizes according to the equation above.

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

   \[
   \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}][\text{H}_2\text{O}]} = \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}
   \]

   (b) Calculate the pH of a 0.25 \( M \) solution of HCOOH.

   \[
   \begin{align*}
   \text{HCOOH} & \quad \text{H}_2\text{O} \\
   \text{H}_3\text{O}^+ & \quad \text{HCOO}^- \\
   \text{H}_2\text{O}^+ & \quad \text{HCOOH} \\
   \end{align*}
   \]

   \[
   \frac{x^2}{0.25} = 1.8 \times 10^{-4} \quad \Rightarrow \quad x = 1.0067
   \]

   \[
   \text{pH} = -\log(0.0067) = 2.47 \quad \approx \quad 2.2
   \]
Continue your response to **QUESTION 1** on this page.

(c) In the box below, complete the Lewis electron-dot diagram for $\text{HCOOH}$. Show all bonding and nonbonding valence electrons.

\[
\begin{array}{c}
\text{O} \\
\text{II} \\
\text{H} - \text{C} - \text{O} - \text{H}
\end{array}
\]

\[
\text{H}_2\text{NNH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{NNH}_2^+(aq) + \text{OH}^-(aq) \quad K_b = 1.3 \times 10^{-6}
\]

(d) In aqueous solution, the compound $\text{H}_2\text{NNH}_2$ reacts according to the equation above. A 50.0 mL sample of 0.25 M $\text{H}_2\text{NNH}_2(aq)$ is combined with a 50.0 mL sample of 0.25 M $\text{HCOOH}(aq)$.

(i) Write the balanced net ionic equation for the reaction that occurs when $\text{H}_2\text{NNH}_2$ is combined with $\text{HCOOH}$.

\[
\text{H}_2\text{NNH}_2 + \text{HCOOH} \rightarrow \text{H}_2\text{NNHCOOH} \quad \text{H}_2\text{NNH}_2\text{COOH}_2
\]

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

The resulting solution is neutral because two conjugate bases come together, one being a weak base and one being a weak acid. Since both are weak and have the same number of moles, the resulting pH is neutral.
When a catalyst is added to a solution of HCOOH\((aq)\), the reaction represented by the following equation occurs.

\[
\text{HCOOH}(aq) \rightarrow \text{H}_2(g) + \text{CO}_2(g)
\]

(e) Is the reaction a redox reaction? Justify your answer.

No, the oxidation numbers do not change throughout the reaction.

(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of \(\text{CO}_2(g)\) produced in the reaction. (Assume that the amount of \(\text{CO}_2(g)\) dissolved in the solution is negligible.)

\[
\frac{n}{M} = \frac{44.01}{22.4} \quad T = 298 \quad R = 0.08206
\]

\[
P \cdot V = n \cdot R \cdot T
\]

\[
(24)(4.3) = n(0.08206)(298)
\]

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

The catalyst will not be used up over time. When the reactants are depleted and the reaction stops, the catalyst will stop.
Question 1

Note: Student samples are quoted verbatim and may contain spelling and grammatical errors.

Overview

Question 1 presents a suite of questions on the reactions and structure of methanoic acid, HCOOH. Part (a) asks the student to write the equilibrium constant expression for the acid ionization reaction of HCOOH. This question addresses Learning Objective SAP-9.C and Science Practice 5.B from the AP Chemistry Course and Exam Description. The $K_a$ expression is used in part (b) to calculate the pH of a solution of HCOOH of known concentration. Two points are possible: one for determining the concentration of $\text{H}_3\text{O}^+$ (SAP-9.C, 5.A) and one for the correct pH (SAP-9.C, 5.F). Part (c) then asks for a drawing of the complete Lewis diagram for HCOOH (SAP-4.A, 3.B).

Methanoic acid reacts with hydrazine ($\text{H}_2\text{NNH}_2$) in an acid-base reaction that the student must describe with a net ionic equation in part (d)(i) (TRA-1.B, 5.E). In part (d)(ii), the student determines whether the resulting solution is acidic, basic, or neutral and explains why (SAP-9.D, 6.D).

Methanoic acid also undergoes a decomposition reaction in the presence of a catalyst. In part (e), the student must determine, with evidence, if it is a redox reaction (TRA-2.A, 6.D). The $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ products increase the total pressure inside the reaction vessel, as shown in a graph. The student needs to calculate the total number of moles of $\text{CO}_2$ produced in the reaction in part (f). This part is worth two points: one for the correct pressure of $\text{CO}_2$ (SPQ-4.A, 5.F), and one for the correct number of moles of $\text{CO}_2$ (SAP-7.A, 5.F). As a follow-up, part (g) asks about how (if at all) the amount of catalyst changes as the reaction proceeds (ENE-1.A, 1.B).

Sample: 1A

Score: 10

This response earned 10 points. In part (a) 1 point was earned for the correct $K_a$ expression. Part (b) earned 2 points; the first point was earned for the correct $[\text{H}_3\text{O}^+]$ with work and the second point was earned for the correct pH. Part (c) earned 1 point for the correct Lewis diagram. Part (d)(i) earned 1 point for the correct net ionic equation. Part (d)(ii) earned 1 point for correctly stating that the solution is acidic, with correct justification. Part (e) earned 1 point for correctly stating that this is a redox reaction and justifying the answer in terms of oxidation numbers. Part (f) earned 2 points; the first point was earned for the correct stoichiometry/partial pressure of $\text{CO}_2$ and the second point was earned for correctly calculating the number of moles of $\text{CO}_2$ using the ideal gas law. Part (g) earned 1 point for correctly stating that the amount of catalyst remains the same, with valid justification.

Sample: 1B

Score: 7

This response earned 7 points. In part (a) 1 point was earned for the correct $K_a$ expression. Part (b) earned 2 points; the first point was earned for the correct $[\text{H}_3\text{O}^+]$ with work and the second point was earned for the correct pH. Part (c) earned 1 point for the correct Lewis diagram. Part (d)(i) earned 1 point for the net ionic equation. Part (d)(ii) earned 0 points for incorrectly stating that the solution is neutral. Part (e) earned 0 points for incorrectly stating that this is not a redox reaction. Part (f) earned 1 point; the first point was not earned because the stoichiometry/partial pressure of $\text{CO}_2$ is not addressed but the second point was earned for correctly calculating the total moles of gas (consistent with the incorrect partial pressure of $\text{CO}_2$) using the ideal gas law. Part (g) earned 1 point for correctly stating that the amount of catalyst remains the same, with valid justification.
Question 1 (continued)

Sample: 1C
Score: 4

This response earned 4 points. In part (a) 0 points were earned due to the omission of “$K_a = \text{ or } 1.8 \times 10^{-4}$.” Part (b) earned 2 points; the first point was earned for the correct $[\text{H}_3\text{O}^+]$ with work and the second point was earned for the correct pH. Part (c) earned 1 point for the correct Lewis diagram. Part (d)(i) earned 0 points for an incorrect net ionic equation. Part (d)(ii) earned 0 points for incorrectly stating that the solution is neutral. Part (e) earned 0 points for incorrectly stating that this is not a redox reaction. Part (f) earned 1 point; the first point was not earned because the stoichiometry/partial pressure of CO$_2$ is not addressed, and the second point was earned for correctly calculating the total number of moles of gas using the ideal gas law. Part (g) earned 0 points because the response includes an invalid justification.