Info about Strong Acids you need to know!

- Dissociate 100% (completely)
- Use your pH equations immediately
- Strong Electrolytes (conduct electricity)
- Greater # of oxygens = stronger the acid
What is the difference between these theories on acids and bases?

<table>
<thead>
<tr>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrhenius</td>
<td></td>
</tr>
<tr>
<td>Bronsted-Lowry</td>
<td></td>
</tr>
</tbody>
</table>

Jan 31-9:18 AM

Bronsted-Lowry  Our most common acids/bases
- Show that HCHO$_2$ has a pH below 7.
- Show that H$_2$NNH$_2$ has a pH above 7.

Jan 31-10:41 AM

Give the conjugate bases of:
- HClO$_3$
- H$_2$S
- HCO$_3^-$
- HCO$_2^-$

Jan 31-10:43 AM
Give the conjugate acids of:

- $\text{SO}_4^{2-}$
- $\text{HSO}_3^-
- \text{NH}_3$
- $\text{H}_2\text{O}$

Feb 1-8:32 AM

EQUILIBRIUM

$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25°C

$= K_a \times K_b$

$p\text{H} = -\log[\text{H}^+]$, $p\text{OH} = -\log[\text{OH}^-]$

$14 = p\text{H} + p\text{OH}$

$p\text{H} = pK_a + \log[A^-]$;
$pK_a = -\logK_a$; $pK_b = -\logK_b$
Calculate the pH of the following solutions

- $8.5 \times 10^{-3} \, M \, HBr$
- A 500mL solution that contains $7.5 \times 10^{-5}$ moles of HCl.
- $0.2 \, \text{mol L}^{-1} \, \text{HNO}_3$ in 250 mL of water.

Calculate the pH of the following solutions

- $1.5 \times 10^{-2} \, M \, \text{NaOH}$
- A 500mL solution that contains $3.0 \times 10^{-3}$ moles of KOH.
- 5 grams of NaOH (FW=40) in 250 mL of water.
Calculate the pH of the following solutions

- Mixing 100 mL of 0.002M HNO₃ with 100mL of 0.001M HNO₃
- Mixing 10 mL of 0.005M NaOH with 40mL of 0.0025M KOH

Calculate the pH of the following solutions

- 50mL of a 0.04M solution of HBr is added to 50mL of water.
- When you dilute an acid like above, is it correct to add an acid to water or should you add water to an acid? Explain in terms of thermodynamics.

Calculate the pH of the following solutions

- \(3.5 \times 10^{-3}\) M HNO₃
- \(1.5 \times 10^{-2}\) M LiOH
- 2 grams of NaOH (FW=40) in 500 mL of water.
- Mixing 20 mL of 0.005M HCl with 80mL of 0.003M HCl
- 10mL of a 6 M solution of HCl is added to 500mL of water.
Hydrazine is an inorganic compound with the formula N₂H₄.

(a) In the box below, complete the Lewis electron-dot diagram for the N₂H₄ molecule by drawing in all the electron pairs.

(b) On the basis of the diagram you completed in part (a), do all six atoms in the N₂H₄ molecule lie in the same plane? Explain.

(c) The normal boiling point of N₂H₄ is 114°C whereas the normal boiling point of C₂H₆ is -89°C. Explain, in terms of the intermolecular forces present in each liquid, why the boiling point of N₂H₄ is so much higher than that of C₂H₆.

(d) Write a balanced chemical equation for the reaction between N₂H₄ and H₂O that explains why a solution of hydrazine in water has a pH greater than 7.

N₂H₄ reacts in air according to the equation below.

N₂H₄(g) + O₂(g) → N₂(g) + 2 H₂O(g) \hspace{1cm} \Delta H^\circ = -534 \text{ kJ mol}^{-1}

(e) Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

(f) Predict the sign of the entropy change, \( \Delta S \), for the reaction. Justify your prediction.

(g) Indicate whether the statement written in the box below is true or false. Justify your answer.

The large negative \( \Delta H^\circ \) for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

Titrations

\[ M_1V_1 = M_2V_2 \]
answer the following questions about acetylsalicylic acid, the active ingredient in aspirin.

(a) The amount of acetylsalicylic acid in a single aspirin tablet is 125 mg, yet the tablet has a mass of 2.00 g. Calculate the mass percent of acetylsalicylic acid in the tablet.

(b) The elements contained in acetylsalicylic acid are hydrogen, carbon, and oxygen. The combustion of 3.000 g of the pure compound yields 1.200 g of water and 0.300 g of dry carbon dioxide. Calculate the mass, in g, of each element in the 3.000 g sample.

(c) A student dissolved 1.025 g of pure acetylsalicylic acid in distilled water and titrated the resulting solution to the equivalence point using 0.05 M NaOH. Assuming that acetylsalicylic acid has only one ionizable hydrogen, calculate the molar mass of the acid.

Feb 7-10:51 AM

(a) An approximately 0.1 molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.

Chem. dry NaOH, large
250 ml Erlenmeyer flask
Wash bottle filled with distilled water

Analytical balance
Potassium hydrogen phthalate, KHP, a pure solid
A pipette

(a) Briefly describe the steps you would take, using materials listed above, to standardize the NaOH solution.

(b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.

(c) After the NaOH solution has been standardized, it is used to titrate a weak monoprotic acid, HF. The equivalence point is reached when 24.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0.00 mL (clearly label the equivalence point on the curve).
(a) Describe 2 features on the graph that identify HA as a weak acid.
(b) Sketch the titration curve that would result if 25 mL of 0.10 M HCl were used instead of HA.
(c) A 25 mL sample of 0.10 M is titrated with 0.20 M NaOH. What volume of base is needed to reach the equivalence point.

Laboratory Questions
1) The redness and itching of the skin caused by ant bites can be relieved by applying a paste made from water and baking soda.
2) CH$_3$COOH, draw the Lewis dot structure, identify the functional group, and identify the hybridization and geometry around each carbon. Also, prove that it has a pH below 7 through a chemical reaction.
3) To clean up an acid spill, should you use water, a solution of sodium carbonate, or a solution of sodium hydroxide? Explain thoroughly.
4) Hydrazine, N$_2$H$_4$, is an inorganic molecule. Write a balanced chemical reaction between hydrazine and water that shows that it has a pH greater than 7. If during the reaction above some hydrazine vaporizes, what specific intermolecular and intramolecular forces are being broken?
X, Y, and Z are KCl, Na₂CO₃, and MgSO₄ (listed in random order)

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH of an Aqueous Solution of the Compound</th>
<th>Result of Adding 1.0 M NaOH to a Solution of the Compound</th>
<th>Result of Adding 1.0 M HCl to a Solution of the Solid Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>&gt; 7</td>
<td>No observed reaction</td>
<td>Evolution of a gas</td>
</tr>
<tr>
<td>Y</td>
<td>7</td>
<td>No observed reaction</td>
<td>No observed reaction</td>
</tr>
<tr>
<td>Z</td>
<td>7</td>
<td>Formation of a white precipitate</td>
<td>No observed reaction</td>
</tr>
</tbody>
</table>

(a) Identify each compound based on the observations recorded in the table.
Compound X.
Compound Y.
Compound Z.

Dec 10-8:02 AM

Keep Calm
It's Just An Acid-Base Quiz

KEEP CALM BECAUSE I'M BATMAN

Dec 13-8:25 AM

1) List 5 strong acids
2) List 1 strong base
3) Write the chemical equation that shows that CH₃COOH in water has a pH less than 7.
4) What is the conjugate base in problem #3?
5) Write the chemical equation that shows that NH₃ in water has a pH greater than 7.
6) What is the conjugate acid in problem #5?

7) Sketch a titration curve of a weak acid being titrated with a strong base (Show the EP).

8) What is the definition for the equivalence point of a titration?
The pH of a 0.0001 M HNO₃ solution is

(A) 4
(B) 3
(C) 2
(D) 1

Which property is not typically associated with basic solutions?

(A) Feel slippery
(B) React with metals to produce H₂ gas
(C) Have a pH above 7.0
(D) React with solutions containing HCO₃⁻ ions

Questions 178-180: Use the answers below to answer questions 3-5.

(A) Br⁻ (aq)
(B) S²⁻ (aq)
(C) NH₄⁺ (aq)
(D) III (aq)

Would be classified as the conjugate acid of a weak base.

Would be classified as the conjugate base of a strong acid.

Would be classified as weak acid.
A 1.0 L solution contains equimolar amounts of NH₄Cl and NH₃. 10 mL of water is added to the solution. Which statement describes the effect of the added water?

(A) The pH increases.
(B) The pH decreases.
(C) The pH remains unchanged.
(D) The molar concentration of the NH₃ increases.

Questions 182-184
Select from the answers below for questions 7-9.

(A) the number of moles present per liter
(B) the molality of the solution
(C) the extent of the dissociation of the electrolytes
(D) inter-ionic attractions

Which of the above is most closely related to the distinction between strong acids and weak acids?

Which of the above is most closely related to the distinction between concentrated and dilute acid solutions?

Which of the above accounts for a pH of 2 for 0.01M HCl, but a pH of 4 for 0.0001 M HCl?

What is the pH of a solution made by adding 200 ml of distilled water to 100 ml of 0.0030 M HNO₃? (Assume volumes are additive.)

(A) 3.0
(B) 2.7
(C) 2.0
(D) 1.0

Questions 186-188
Choose from the answers below to answer questions 11-13.

(A) KOH
(B) NaHSO₄
(C) C₂H₅OH
(D) NH₃

Which of the above aqueous solutions is an example of a Bronsted-Lowry acid?

Which of the above aqueous solutions would be classified as neither a Bronsted-Lowry acid nor a base?

Which of the above 0.1M aqueous solutions would have the highest pH?
A student pipettes 25.00 mL samples of HCl solution into separate Erlenmeyer flasks, dilutes the acid with 20 mL of distilled water and adds 3 drops of phenolphthalein to each flask. The solutions are titrated with NaOH from a buret until a pale pink color persists. The following data are recorded.

Volumes of NaOH solution added

Trial #1 32.25 mL  
Trial #2 33.50 mL  
Trial #3 33.49 mL  
Trial #4 33.51 mL

Which statement below is the most probably explanation for the student’s results?

(A) The student added too little phenolphthalein to the first solution.  
(B) A different amount of water was added to the first flask.  
(C) The buret was not rinsed with NaOH solution before filling.  
(D) The pipet was not rinsed with HCl before filling.

Questions 75-77: Choose from the answers below to answer questions 15-17.

Consider 100 mL of each solution,

(A) 0.1 M NaOH  
(B) 0.2 M NaCl  
(C) 0.1 M NaC₂H₃O₂  
(D) 0.1 M AlCl₃

190 Which solution would be expected to have the lowest pH?

191 Which solution would have a pH closest to pH = 8.2?

192 Which solution pH will remain the same if 50 mL of distilled water is added to each solution?

193 Which statement is true?

(A) The outer limits of the pH scale are 0 and 14.  
(B) The weaker the acid, the more strongly its salts hydrolyze.  
(C) The pH of a neutral solution is always 7.  
(D) A solution of HNO₃ can be made basic if enough water is added.
194 49. If the dissociation of water, $H_2O \leftrightarrow H^+ + OH^-$ is endothermic, and some room temperature water is heated to boiling, which of the following is true?

(A) The pH will be 7; the solution will be acidic.
(B) The pH will be greater than 7, but the solution will be neutral.
(C) The pH will be less than 7, but the solution will be neutral.
(D) The pH will be less than 7; the pOH will be less than 7, and the solution will be acidic.

195-196

Questions 26-29:

(A) Spectrophotometric (color) analysis
(B) Mass spectroscopy analysis
(C) Photon emission spectroscopy (PES)
(D) Titration with a pH meter (probe)

195 30. Which method would most likely be used to determine the molar mass of an unknown solid monoprotic acid?

196 31. Which method would most likely be used to determine the wavelength of maximum absorbance for an aqueous CuSO$_4$ solution?

197 32. A 20.0 mL sample of a weak acid, HX is titrated to the endpoint and requires 50.0 mL of a 0.050 M KOH solution. After the addition of the first 30.0 mL of KOH, the pH of the solution is 5.00. What is the dissociation constant, $K_a$, for this weak acid, HX?

(A) $1.5 \times 10^{-5}$
(B) $2.0 \times 10^{-6}$
(C) $3.0 \times 10^{-6}$
(D) $6.7 \times 10^{-6}$

198-199

Questions 23-24: Select from the answers below to answer questions 23–24.

(A) 0.0
(B) 1.0
(C) 2.0
(D) 12

198 23. The pH of a 1.0 M solution of HI

199 24. The pH of a 0.01 M solution of KOH
Which equation below illustrates amphoteric behavior of Al(OH)$_3$?

(A) Al$^{3+}$(aq) + 6H$_2$O(l) $\rightarrow$ Al(H$_2$O)$_6^{3+}$(aq)
(B) Al(H$_2$O)$_6^{3+}$(aq) + H$_2$O(l) $\rightarrow$ H$_3$O$^+$(aq) + Al(H$_2$O)$_5$OH$^{2+}$(aq)
(C) Al(OH)$_3$(s) $\rightarrow$ Al$^{3+}$(aq) + 3OH$^-$(aq)
(D) Al(OH)$_3$(s) + OH$^-$(aq) $\rightarrow$ Al(OH)$_4^-$(aq)
1999

CHEMISTRY

SECTION II

(Total time—90 minutes)

Part A

Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in this booklet.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

1. In aqueous solution, ammonia reacts as represented above. In 0.0180 \( M \) \( \text{NH}_3(aq) \) at 25°C, the hydroxide ion concentration, \([\text{OH}^-]\), is \( 5.60 \times 10^{-3} \) \( M \). In answering the following, assume that temperature is constant at 25°C and that volumes are additive.

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

(b) Determine the pH of 0.0180 \( M \) \( \text{NH}_3(aq) \).

(c) Determine the value of the base ionization constant, \( K_b \), for \( \text{NH}_3(aq) \).

(d) Determine the percent ionization of \( \text{NH}_3 \) in 0.0180 \( M \) \( \text{NH}_3(aq) \).

(e) In an experiment, a 20.0 mL sample of 0.0180 \( M \) \( \text{NH}_3(aq) \) was placed in a flask and titrated to the equivalence point and beyond using 0.0120 \( M \) \( \text{HCl}(aq) \).

(i) Determine the volume of 0.0120 \( M \) \( \text{HCl}(aq) \) that was added to reach the equivalence point.

(ii) Determine the pH of the solution in the flask after a total of 15.0 mL of 0.0120 \( M \) \( \text{HCl}(aq) \) was added.

(iii) Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 \( M \) \( \text{HCl}(aq) \) was added.
8. A volume of 30.0 mL of 0.10 M NH₃(aq) is titrated with 0.20 M HCl(aq). The value of the base-dissociation constant, $K_b$, for NH₃ in water is $1.8 \times 10^{-5}$ at 25°C.

(a) Write the net-ionic equation for the reaction of NH₃(aq) with HCl(aq).

(b) Using the axes provided below, sketch the titration curve that results when a total of 40.0 mL of 0.20 M HCl(aq) is added dropwise to the 30.0 mL volume of 0.10 M NH₃(aq).

(c) From the table below, select the most appropriate indicator for the titration. Justify your choice.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Red</td>
<td>5.5</td>
</tr>
<tr>
<td>Bromothymol Blue</td>
<td>7.1</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.7</td>
</tr>
</tbody>
</table>

(d) If equal volumes of 0.10 M NH₃(aq) and 0.10 M NH₄Cl(aq) are mixed, is the resulting solution acidic, neutral, or basic? Explain.

END OF EXAMINATION

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3. Answer the following questions about acetylsalicylic acid, the active ingredient in aspirin.

(a) The amount of acetylsalicylic acid in a single aspirin tablet is 325 mg, yet the tablet has a mass of 2.00 g. Calculate the mass percent of acetylsalicylic acid in the tablet.

(b) The elements contained in acetylsalicylic acid are hydrogen, carbon, and oxygen. The combustion of 3.000 g of the pure compound yields 1.200 g of water and 3.72 L of dry carbon dioxide, measured at 750. mm Hg and 25°C. Calculate the mass, in g, of each element in the 3.000 g sample.

(c) A student dissolved 1.625 g of pure acetylsalicylic acid in distilled water and titrated the resulting solution to the equivalence point using 88.43 mL of 0.102 M NaOH(aq). Assuming that acetylsalicylic acid has only one ionizable hydrogen, calculate the molar mass of the acid.

(d) A $2.00 \times 10^{-3}$ mole sample of pure acetylsalicylic acid was dissolved in 15.00 mL of water and then titrated with 0.100 M NaOH(aq). The equivalence point was reached after 20.00 mL of the NaOH solution had been added. Using the data from the titration, shown in the table below, determine

(i) the value of the acid dissociation constant, $K_a$, for acetylsalicylic acid and

(ii) the pH of the solution after a total volume of 25.00 mL of the NaOH solution had been added (assume that volumes are additive).

<table>
<thead>
<tr>
<th>Volume of 0.100 M NaOH Added (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.22</td>
</tr>
<tr>
<td>5.00</td>
<td>2.97</td>
</tr>
<tr>
<td>10.00</td>
<td>3.44</td>
</tr>
<tr>
<td>15.00</td>
<td>3.92</td>
</tr>
<tr>
<td>20.00</td>
<td>8.13</td>
</tr>
<tr>
<td>25.00</td>
<td>?</td>
</tr>
</tbody>
</table>
2003 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY
Section II
(Total time—90 minutes)

Part A
Time—40 minutes
YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

C₆H₅NH₂(aq) + H₂O(l) ⇌ C₆H₅NH₃⁺(aq) + OH⁻(aq)

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

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

(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.

(c) The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.

(d) Calculate the pH at the equivalence point of the titration in part (c).

(e) The pK_a values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erythrosine</td>
<td>3</td>
</tr>
<tr>
<td>Litmus</td>
<td>7</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>10</td>
</tr>
</tbody>
</table>
2004 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

Answer BOTH Question 5 below AND Question 6 printed on page 11. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

5. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

(a) What measurement(s) must be made to determine the number of moles of NaOH used in the titration?

(b) Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.

(c) How can the number of moles of HA consumed in the titration be determined?

(d) In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA?

(e) Write the mathematical expression that is used to determine the molar mass of HA.

(f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.

(g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

(ii) The procedure called for 25 mL of H₂O in the Erlenmeyer flask, but a student used 35 mL of H₂O.

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GO ON TO THE NEXT PAGE.
2005 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

CHEMISTRY
Section II
(Total time—90 minutes)

Part A
Time—40 minutes
YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in this booklet. Do NOT write your answers on the lavender insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

\[ K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = 3.2 \times 10^{-8} \]

1. Hypochlorous acid, HOCl, is a weak acid in water. The \( K_a \) expression for \( \text{HOCl} \) is shown above.

   (a) Write a chemical equation showing how \( \text{HOCl} \) behaves as an acid in water.

   (b) Calculate the pH of a 0.175 \( M \) solution of \( \text{HOCl} \).

   (c) Write the net ionic equation for the reaction between the weak acid \( \text{HOCl(aq)} \) and the strong base \( \text{NaOH(aq)} \).

   (d) In an experiment, 20.00 mL of 0.175 \( M \) \( \text{HOCl(aq)} \) is placed in a flask and titrated with 6.55 mL of 0.435 \( M \) \( \text{NaOH(aq)} \).

      (i) Calculate the number of moles of \( \text{NaOH(aq)} \) added.

      (ii) Calculate \( [H_3O^+] \) in the flask after the \( \text{NaOH(aq)} \) has been added.

      (iii) Calculate \( [\text{OH}^-] \) in the flask after the \( \text{NaOH(aq)} \) has been added.
2005 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY
Section II
(Total time—90 minutes)

Part A
Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

\[
\text{HC}_3\text{H}_5\text{O}_2(aq) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}^+(aq) \quad K_a = 1.34 \times 10^{-5}
\]

1. Propanoic acid, HC\textsubscript{3}H\textsubscript{5}O\textsubscript{2}, ionizes in water according to the equation above.

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

(b) Calculate the pH of a 0.265 M solution of propanoic acid.

(c) A 0.496 g sample of sodium propanoate, NaC\textsubscript{3}H\textsubscript{5}O\textsubscript{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, C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}^- (aq), in the solution

(ii) The concentration of the H\textsuperscript{+}(aq) ion in the solution

The methanoate ion, HCO\textsubscript{2}^- (aq), reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.

\[
\text{HCO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_2\text{H}(aq) + \text{OH}^-(aq)
\]

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

(i) The value of \( K_b \) for the methanoate ion, HCO\textsubscript{2}^- (aq)

(ii) The value of \( K_a \) for methanoic acid, HCO\textsubscript{2}H

(e) Which acid is stronger, propanoic acid or methanoic acid? Justify your answer.
C\textsubscript{6}H\textsubscript{5}COOH(s) \rightleftharpoons C\textsubscript{6}H\textsubscript{5}COO\textsuperscript{-}(aq) + H\textsuperscript{+}(aq) \quad K_a = 6.46 \times 10^{-5}

1. Benzoic acid, C\textsubscript{6}H\textsubscript{5}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) [H\textsuperscript{+}] in the solution
(ii) [OH\textsuperscript{-}] in the solution
(iii) The number of moles of NaOH added
(iv) The number of moles of C\textsubscript{6}H\textsubscript{5}COO\textsuperscript{-}(aq) in the solution
(v) The number of moles of C\textsubscript{6}H\textsubscript{5}COOH in the solution

(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

In a different titration, a 0.7529 g sample of a mixture of solid C\textsubscript{6}H\textsubscript{5}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
(ii) The mass percentage of benzoic acid in the solid sample
Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. Answer the following questions about laboratory situations involving acids, bases, and buffer solutions.

(a) Lactic acid, \(\text{HC}_3\text{H}_5\text{O}_3\), reacts with water to produce an acidic solution. Shown below are the complete Lewis structures of the reactants.

\[
\begin{align*}
\text{H} & \\
\text{H} : \text{O} : : \text{O} & \\
\text{H} - \text{C} - \text{C} - \text{O} & \quad + \\
\text{H} & \\
\end{align*}
\]

In the space provided above, complete the equation by drawing the complete Lewis structures of the reaction products.

(b) Choosing from the chemicals and equipment listed below, describe how to prepare 100.00 mL of a 1.00 \(M\) aqueous solution of \(\text{NH}_4\text{Cl}\) (molar mass 53.5 g \(\text{mol}^{-1}\)). Include specific amounts and equipment where appropriate.

<table>
<thead>
<tr>
<th>(\text{NH}_4\text{Cl(s)})</th>
<th>50 mL buret</th>
<th>100 mL graduated cylinder</th>
<th>100 mL pipet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>100 mL beaker</td>
<td>100 mL volumetric flask</td>
<td>Balance</td>
</tr>
</tbody>
</table>

(c) Two buffer solutions, each containing acetic acid and sodium acetate, are prepared. A student adds 0.10 mol of \(\text{HCl}\) to 1.0 L of each of these buffer solutions and to 1.0 L of distilled water. The table below shows the pH measurements made before and after the 0.10 mol of \(\text{HCl}\) is added.

<table>
<thead>
<tr>
<th></th>
<th>pH Before HCl Added</th>
<th>pH After HCl Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>7.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Buffer 1</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Buffer 2</td>
<td>4.7</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(i) Write the balanced net-ionic equation for the reaction that takes place when the \(\text{HCl}\) is added to buffer 1 or buffer 2.

(ii) Explain why the pH of buffer 1 is different from the pH of buffer 2 after 0.10 mol of \(\text{HCl}\) is added.

(iii) Explain why the pH of buffer 1 is the same as the pH of buffer 2 before 0.10 mol of \(\text{HCl}\) is added.
CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

\[ \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \quad K_a = 7.2 \times 10^{-4} \]

1. Hydrofluoric acid, HF(aq), dissociates in water as represented by the equation above.

(a) Write the equilibrium-constant expression for the dissociation of HF(aq) in water.

(b) Calculate the molar concentration of \( \text{H}_3\text{O}^+ \) in a 0.40 \( M \) HF(aq) solution.

HF(aq) reacts with NaOH(aq) according to the reaction represented below.

\[ \text{HF}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{F}^-(aq) \]

A volume of 15 mL of 0.40 \( M \) NaOH(aq) is added to 25 mL of 0.40 \( M \) HF(aq) solution. Assume that volumes are additive.

(c) Calculate the number of moles of HF(aq) remaining in the solution.

(d) Calculate the molar concentration of F\(^-\)(aq) in the solution.

(e) Calculate the pH of the solution.
2009 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

CHEMISTRY
Section II
(Total time—95 minutes)

Part A
Time—55 minutes
YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS.
It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if
you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in this booklet. Do
NOT write your answers on the lavender insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. A pure 14.85 g sample of the weak base ethylamine, C$_2$H$_5$NH$_2$, is dissolved in enough distilled water to make
500. mL of solution.

(a) Calculate the molar concentration of the C$_2$H$_5$NH$_2$ in the solution.

The aqueous ethylamine reacts with water according to the equation below.

$$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$$

(b) Write the equilibrium-constant expression for the reaction between C$_2$H$_5$NH$_2(aq)$ and water.

(c) Of C$_2$H$_5$NH$_2(aq)$ and C$_2$H$_5$NH$_3^+(aq)$, which is present in the solution at the higher concentration at
equilibrium? Justify your answer.

(d) A different solution is made by mixing 500. mL of 0.500 M C$_2$H$_5$NH$_2$ with 500. mL of 0.200 M HCl.
Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

(i) Calculate the concentration of OH$^-(aq)$ in the solution.

(ii) Write the net-ionic equation that represents the reaction that occurs when the C$_2$H$_5$NH$_2$ solution is
mixed with the HCl solution.

(iii) Calculate the molar concentration of the C$_2$H$_5$NH$_3^+(aq)$ that is formed in the reaction.

(iv) Calculate the value of $K_b$ for C$_2$H$_5$NH$_2$. 

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1. Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$ at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>HOBr</td>
<td>$2.4 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

(i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of $K_a$.

(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $\text{OCl}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^- (aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $\text{OCl}^- (aq)$ and $\text{H}_2\text{O}(l)$.

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

(iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K.
(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of
the buffer solution is determined to be 6.48.

(i) Calculate the value of $[H_3O^+]$ in the buffer solution.

(ii) Indicate which of HOCl$(aq)$ or OCl$^-(aq)$ is present at the higher concentration in the buffer solution.
Support your answer with a calculation.

2. A student was assigned the task of determining the molar mass of an unknown gas. The student measured the
mass of a sealed 843 mL rigid flask that contained dry air. The student then flushed the flask with the unknown
gas, resealed it, and measured the mass again. Both the air and the unknown gas were at 23.0°C and 750. torr.
The data for the experiment are shown in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Volume of sealed flask</th>
<th>Mass of sealed flask and dry air</th>
<th>Mass of sealed flask and unknown gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>843 mL</td>
<td>157.70 g</td>
<td>158.08 g</td>
</tr>
</tbody>
</table>

(a) Calculate the mass, in grams, of the dry air that was in the sealed flask. (The density of dry air is 1.18 g L$^{-1}$
at 23.0°C and 750. torr.)

(b) Calculate the mass, in grams, of the sealed flask itself (i.e., if it had no air in it).

(c) Calculate the mass, in grams, of the unknown gas that was added to the sealed flask.

(d) Using the information above, calculate the value of the molar mass of the unknown gas.

After the experiment was completed, the instructor informed the student that the unknown gas was carbon
dioxide (44.0 g mol$^{-1}$).

(e) Calculate the percent error in the value of the molar mass calculated in part (d).

(f) For each of the following two possible occurrences, indicate whether it by itself could have been responsible
for the error in the student’s experimental result. You need not include any calculations with your answer.
For each of the possible occurrences, justify your answer.

   Occurrence 1: The flask was incompletely flushed with CO$_2(g)$, resulting in some dry air remaining
                    in the flask.

   Occurrence 2: The temperature of the air was 23.0°C, but the temperature of the CO$_2(g)$ was lower than
                    the reported 23.0°C.

(g) Describe the steps of a laboratory method that the student could use to verify that the volume of the rigid
flask is 843 mL at 23.0°C. You need not include any calculations with your answer.
2011 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

(a) Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH solution.

(b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH solution using 5.000 M NaOH and equipment selected from the list below.

<table>
<thead>
<tr>
<th>Balance</th>
<th>25 mL Erlenmeyer flask</th>
<th>100 mL graduated cylinder</th>
<th>100 mL volumetric flask</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mL buret</td>
<td>100 mL Florence flask</td>
<td>25 mL pipet</td>
<td>100 mL beaker</td>
</tr>
<tr>
<td>Eyedropper</td>
<td>Drying oven</td>
<td>Wash bottle of distilled H₂O</td>
<td>Crucible</td>
</tr>
</tbody>
</table>

(c) The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

(i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

(ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl red</td>
<td>5</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>7</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>9</td>
</tr>
</tbody>
</table>

(d) The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.

(i) What is the value of the acid-dissociation constant, Kₐ, for the weak acid? Explain your reasoning.

(ii) Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.
2011 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY
Section II
(Total time—95 minutes)

Part A
Time—55 minutes
YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH₃, or NH₄Cl, as shown above. Each solution is at 25°C.

(a) Determine the pH of the solution in beaker 1. Justify your answer.

(b) In beaker 2, the reaction \( \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \) occurs. The value of \( K_b \) for \( \text{NH}_3(aq) \) is \( 1.8 \times 10^{-5} \) at 25°C.

(i) Write the \( K_b \) expression for the reaction of \( \text{NH}_3(aq) \) with \( \text{H}_2\text{O}(l) \).

(ii) Calculate the [OH⁻] in the solution in beaker 2.

(c) In beaker 3, the reaction \( \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \) occurs.

(i) Calculate the value of \( K_a \) for \( \text{NH}_4^+(aq) \) at 25°C.

(ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

(d) The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

(i) Is the resulting solution an effective buffer? Justify your answer.

(ii) Calculate the final [NH₄⁺] in the resulting solution at 25°C.
CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in this booklet.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

<table>
<thead>
<tr>
<th>Volume of 0.250 M NaOH Added (mL)</th>
<th>pH of Titrated Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>?</td>
</tr>
<tr>
<td>10.0</td>
<td>3.72</td>
</tr>
<tr>
<td>20.0</td>
<td>4.20</td>
</tr>
<tr>
<td>30.0</td>
<td>?</td>
</tr>
<tr>
<td>40.0</td>
<td>8.62</td>
</tr>
<tr>
<td>50.0</td>
<td>12.40</td>
</tr>
</tbody>
</table>

(a) Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.

(b) Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

(c) Calculate the number of moles of HA that were titrated.

(d) Calculate the molar mass of HA.

The equation for the dissociation reaction of HA in water is shown below.

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^- (aq) \quad K_a = 6.3 \times 10^{-5}
\]

(e) Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 M. Determine the pH of the initial HA solution.

(f) Calculate the value of [H$_3$O$^+$] in the solution after 30.0 mL of NaOH solution is added and the total volume of the solution is 80.0 mL.

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GO ON TO THE NEXT PAGE.
9 Points

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit.
(except for pH: +/- two digits)

(a) \[ K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \] \hspace{1cm} 1 pt

(b) \[[\text{OH}^-] = 5.60 \times 10^{-4} \Rightarrow \left\{ \begin{array}{l}
\text{or} \\
[H^+] = 1.79 \times 10^{-11}
\end{array} \right. \Rightarrow \text{pH} = 10.748 \] \hspace{1cm} 1 pt

(c) \[ K_b = \frac{(5.60 \times 10^{-4})^2}{0.0180 - 5.60 \times 10^{-4}} = 1.74 \times 10^{-5} \text{ (or } 1.80 \times 10^{-5}) \] \hspace{1cm} 2 pts

Note: 1st point for \[[\text{NH}_4^+] = [\text{OH}^-] = 5.60 \times 10^{-4}; 2nd point for correct answer

(d) \% \text{ionization} = \frac{5.60 \times 10^{-4}}{0.0180} \times 100 \% = 3.11\% \text{ (or } 0.0311) \] \hspace{1cm} 1 pt

(e) \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+

(i) \text{mol NH}_3 = 0.0180 \text{ M} \times 0.0200 \text{ L} = 3.60 \times 10^{-4} \text{ mol} = \text{mol H}^+ \text{ needed}

\text{vol HCl solution} = \frac{3.60 \times 10^{-4} \text{ mol}}{0.0120 \text{ M}} = 0.0300 \text{ L} = 30.0 \text{ mL} \hspace{1cm} 1 pt

(ii) \text{mol H}^+ \text{ added} = \text{mol} 0.0120 \text{ M} \times 0.0150 \text{ L} = 1.80 \times 10^{-4} \text{ mol H}^+ \text{ added}

\[ [\text{NH}_4^+] = \frac{1.80 \times 10^{-4} \text{ mol}}{0.0350 \text{ L}} = 0.00514 \text{ M} = [\text{NH}_3] \] \hspace{1cm} 1 pt

Note: Point earned for \(1.80 \times 10^{-4}\) mol, or \(0.00514 \text{ M} \ [\text{NH}_3]\) or \([\text{NH}_4^+]\),
or statement “halfway to equivalence point”.

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Question 1 (cont.)

\[ K_b = 1.80 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{OH}^-] \Rightarrow \text{pOH} = 4.745 \Rightarrow \text{pH} = 9.255 \quad 1 \text{ pt} \]

\[ (= 1.74 \times 10^{-5}) \quad (= 4.759) \quad (= 9.241) \]

(iii) 10.0 mL past equivalence point

\[ 0.0100 \times 0.0120 \, M = 1.20 \times 10^{-4} \, \text{mol H}^+ \text{ in 60.0 mL} \]

\[ [\text{H}^+] = \frac{0.000120 \, \text{mol}}{0.0600 \, \text{L}} = 0.00200 \, M \]

\[ \text{pH} = -\log (2.00 \times 10^{-5}) = 2.700 \quad 1 \text{ pt} \]

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit (except for pH: +/- two digits)
**Question 8**
(8 points)

(a) \( \text{NH}_3(aq) + \text{H}^+(aq) \rightarrow \text{NH}_4^+(aq) \)

or

\( \text{NH}_3(aq) + \text{H}_2\text{O}^+(aq) \rightarrow \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \)

*Note:* phase designations not required to earn point

(b) Sketch of Titration Curve:

3 pts.

- 1\textsuperscript{st} pt. \( \rightarrow \) initial pH must be > 7 (calculated pH ≈ 11)
- 2\textsuperscript{nd} pt. \( \rightarrow \) 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)
- 3\textsuperscript{rd} pt. \( \rightarrow \) 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)
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 \times 10^{-5}) and K_a for NH_4^+ (5.6 \times 10^{-10}) indicate that NH_3 is a
stronger base than NH_4^+ is an acid

or 1 pt.

[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
pOH \approx 5 and pH \approx 9 (i.e., recognition of buffer, so that \log \left( \frac{0.05}{0.05} \right) = 0 \Rightarrow
pOH = pK_b \approx 5 \Rightarrow pH = 14 - pOH \approx 9)
Question 3

(a) \(\frac{0.325 \text{ g}}{2.00 \text{ g}} \times 100\% = 16.2\%\)  
1 point

(b) \(\frac{1.200 \text{ g} \text{ H}_2\text{O}}{18.02 \text{ g/mol}} = 0.06659 \text{ mol} \text{ H}_2\text{O}\) 
\((0.06659 \text{ mol} \text{ H}_2\text{O})(2 \text{ mol} \text{ H/mol} \text{ H}_2\text{O}) = 0.1332 \text{ mol} \text{ H}\) 
\((0.1332 \text{ mol} \text{ H})(1.008 \text{ g/mol} \text{ H}) = 0.1343 \text{ g} \text{ H}\)  
1 point

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

\((0.150 \text{ mol} \text{ CO}_2)(1 \text{ mol} \text{ C/mol} \text{ CO}_2) = 0.150 \text{ mol} \text{ C}\) 
\((0.150 \text{ mol} \text{ C})(12.0 \text{ g/mol}) = 1.80 \text{ g} \text{ C}\)  
1 point

gEchoes, oxygen = 3.00 g - (1.80 g + 0.133 g) = 1.07 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 \(\text{CO}_2\) to moles of \(\text{C}\) and then grams of \(\text{C}\). If the number of moles of \(\text{CO}_2\) 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 \(\text{H}\) and \(\text{C}\) 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) \(\text{moles} \text{ OH}^- = (0.08843 \text{ L})(0.102 \text{ mol/L}) = 0.00902 \text{ mol} \text{ OH}^-\)  
1 point

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

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

Note: The first point is earned for setting up the calculation to determine the number of moles of \(\text{OH}^-\) used in the titration; the second point is earned for using the number of moles of \(\text{OH}^-\) correctly to get the molar mass. If the number of moles of \(\text{OH}^-\) is incorrectly calculated, credit can be earned for this step if the student uses the incorrect value correctly.
Question 3 (cont.)

(d) (i) The $pK_a$ is equal to the pH halfway to the equivalence 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 $\text{OH}^-$, and the $[\text{OH}^-]$ determines the pH.

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

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

$pOH = 1.90$

$pH = 12.10$

Note: The first point is earned for recognizing that the pH past the end point is determined by the amount of excess $\text{OH}^-$ ions; the second point is earned for the calculations and the final answer.
Question 1

\[ C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq) \]

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.

\[
K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} \quad 1 \text{ point for correct expression}
\]

(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.

\[
\begin{align*}
\text{pH} &= 8.82 \\
pOH &= 14 - 8.82 = 5.18 \\
[OH^-] &= 10^{-5.18} = 6.61 \times 10^{-6} M \\
[C_6H_5NH_3^+] &= [OH^-] = 6.6 \times 10^{-6} M \\
K_b &= \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(6.6 \times 10^{-6})^2}{0.10} \\
K_b &= 4.4 \times 10^{-10}
\end{align*}
\]

1 point for calculation of \([OH^-]\)  
1 point for \([C_6H_5NH_3^+] = [OH^-]\)  
1 point for calculation of \(K_b\)

Note: Following this point, any value of \(K_b\) obtained must be carried through.
(c) The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.

\[
\begin{aligned}
n_{C_6H_5NH_2} &= 0.025 L \left( \frac{0.10 \text{ mol}}{1 \text{ L}} \right) = 0.0025 \text{ mol } C_6H_5NH_2 \\
n_{\text{HCl}} &= 0.0050 L \left( \frac{0.10 \text{ mol}}{1 \text{ L}} \right) = 0.00050 \text{ mol HCl (or } H^+) \\
C_6H_5NH_2(aq) + H^+(aq) &\rightleftharpoons C_6H_5NH_3^+(aq) \\
I &\quad 0.0025 \text{ mol} \\
C &\quad -0.00050 \text{ mol} \\
E &\quad 0.0020 \text{ mol} \\
\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq) \\
0.0020 \text{ mol} &\quad = 0.0667 \text{ M} \\
0.030 \text{ L} &\quad = 0.00050 \text{ mol} \\
I &\quad 0.0667 \\
C &\quad -x \\
E &\quad 0.0667 - x \\
\text{K}_b = \frac{[C_6H_5NH_3^+] [OH^-]}{[C_6H_5NH_2]} = 4.37 \times 10^{-10} \\
4.37 \times 10^{-10} = \frac{(0.0167 + x)(x)}{(0.0667 - x)} \\
\text{assume that } x \ll 0.0667 \text{ M: } 4.37 \times 10^{-10} = \frac{(0.0167)x}{0.0667} \\
x = [OH^-] = 1.75 \times 10^{-9} \text{ M} \\
pOH = -\log (1.75 \times 10^{-9}) = 8.76 \\
pH = 14 - 8.76 = 5.24 \\
\text{OR} \\
pOH = pK_b + \log \frac{[C_6H_5NH_3^+]}{[C_6H_5NH_2]} \\
pOH = -\log (4.37 \times 10^{-10}) + \log \frac{0.0167}{0.0667} \\
pOH = 9.36 + \log 0.25 \\
pOH = 9.36 + (-0.60) = 8.76 \\
pH = 14 - 8.76 = 5.24
\end{aligned}
\]
Question 1 (cont’d.)

(d) Calculate the pH at the equivalence point of the titration in part (c).

At the equivalence point, moles of C₆H₅NH₂ = moles of H⁺

\[ C₆H₅NH₂(\text{aq}) + H⁺(\text{aq}) \rightleftharpoons C₆H₅NH₃⁺(\text{aq}) \]

\[
\begin{array}{ccc}
\text{I} & 0.0025 \text{ mol} & 0.0025 \text{ mol} & 0 \text{ mol} \\
\text{C} & -0.0025 & -0.0025 & +0.0025 \\
\text{E} & 0 & 0 & 0.0025
\end{array}
\]

Need 25 mL of 0.1 M HCl to reach the equivalence point of this titration. The total volume of the solution is 50.0 mL.

\[ [C₆H₅NH₃⁺] = \frac{0.0025 \text{ mol}}{0.050 \text{ L}} = 0.050 \text{ M} \]

\[ C₆H₅NH₃⁺(\text{aq}) \rightleftharpoons C₆H₅NH₂(\text{aq}) + H⁺(\text{aq}) \]

\[
\begin{array}{ccc}
\text{I} & 0.050 \text{ M} & 0 & 0 \\
\text{C} & -x & +x & +x \\
\text{E} & 0.050 - x & x & x
\end{array}
\]

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-10}} = 2.3 \times 10^{-5} \]

\[ \frac{[C₆H₅NH₂][H⁺]}{[C₆H₅NH₃⁺]} = 2.3 \times 10^{-5} = \frac{(x)(x)}{(0.050 - x)} \]

assume that \( x \ll 0.050 \text{ M} \): \( 2.3 \times 10^{-5} = \frac{(x)(x)}{0.050} \)

\[ x = [H⁺] = 1.1 \times 10^{-3} \text{ M} \]

\[ \text{pH} = 2.96 \]

(e) The pKₐ values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erythrosine</td>
<td>3</td>
</tr>
<tr>
<td>Litmus</td>
<td>7</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>10</td>
</tr>
</tbody>
</table>

The pH at the equivalence point is acidic. The best indicator is erythrosine, for which the value of pKₐ is closest to the pH at the equivalence point.
5. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

(a) What measurement(s) must be made to determine the number of moles of NaOH used in the titration?

Initial volume of standardized NaOH solution and final volume of standardized NaOH solution (volume at the endpoint of the titration)  
1 point for identifying both initial and final volume of base

(b) Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.

\[ M_{NaOH} \times V_{NaOH} \]  
(Molarity of NaOH solution) times (volume (in L) of NaOH added)  
1 point for mathematical expression

(c) How can the number of moles of HA consumed in the titration be determined?

\[ HA + NaOH \rightarrow NaA + H_2O \]  
moles HA = moles NaOH  
moles monoprotic acid = moles NaOH  
\[ n_{HA} = moles \ NaOH \left( \frac{1 \ mol \ HA}{1 \ mol \ NaOH} \right) \]  
1 point for showing conversion based on stoichiometry of the neutralization reaction

(d) In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA?

mass of HA  
1 point for measurement

(e) Write the mathematical expression that is used to determine the molar mass of HA.

\[ \frac{\text{mass HA}}{\text{mol HA}} \]  
mass of HA measured in part (d) divided by the moles of HA determined in part (c)  
1 point for quotient
(f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.

Chemicals needed in flask: solid weak monoprotic acid (HA) and an indicator to detect endpoint of titration
Chemical in buret: standardized NaOH solution

1 point for either one of two chemicals in flask, 2 points for both
1 point for NaOH in the buret

(g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

Measured mass of HA is larger; so, according to expression in part (e), calculated molar mass will be higher than it should.

1 point for the effect on molar mass and explanation.

(ii) The procedure called for 25 mL of H₂O in the Erlenmeyer flask, but a student used 35 mL of H₂O.

No effect on calculated molar mass, because mathematical expression for molar mass does not include amount of water used to dissolve solid HA. Both mass and number of moles of HA are unaffected by the addition of water.

1 point for effect on molar mass and explanation.
Hypochlorous acid, HOCl, is a weak acid in water. The $K_a$ expression for HOCl is shown above.

(a) Write a chemical equation showing how HOCl behaves as an acid in water.

$$\text{HOCl(aq) + H}_2\text{O(l)} \rightarrow \text{OCl}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)} \quad \text{One point is earned for the correct chemical equation.}$$

(b) Calculate the pH of a 0.175 M solution of HOCl.

$$\begin{align*}
\text{HOCl(aq) + H}_2\text{O(l)} &\rightleftharpoons \text{OCl}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)} \\
\text{I} &\quad 0.175 \quad - \quad 0 \quad \sim 0 \\
\text{C} &\quad -x \quad - \quad +x \quad +x \\
\text{E} &\quad 0.175 - x \quad - \quad +x \quad +x
\end{align*}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(x)}{(0.175-x)}$$

Assume that $0.175 - x \approx 0.175$

$$3.2 \times 10^{-8} = \frac{x^2}{0.175}$$

$$x^2 = (3.2 \times 10^{-8})(0.175) = 5.6 \times 10^{-9}$$

$$x = [\text{H}_3\text{O}^+] = 7.5 \times 10^{-5} \text{M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.5 \times 10^{-5}) = 4.13$$

(c) Write the net ionic equation for the reaction between the weak acid HOCl(aq) and the strong base NaOH(aq).

$$\text{HOCl(aq) + OH}^-\text{(aq)} \rightarrow \text{OCl}^-\text{(aq)} + \text{H}_2\text{O(l)} \quad \text{One point is earned for both of the correct reactants.}$$

(d) In an experiment, 20.00 mL of 0.175 M HOCl(aq) is placed in a flask and titrated with 6.55 mL of 0.435 M NaOH(aq).

(i) Calculate the number of moles of NaOH(aq) added.

$$\begin{align*}
\text{mol}_{\text{NaOH}} &= 6.55 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} \times \frac{0.435 \text{ mol NaOH}}{1 \text{ L}} \\
\text{mol}_{\text{NaOH}} &= 2.85 \times 10^{-3} \text{ mol NaOH} \quad \text{One point is earned for the correct number of moles of NaOH.}
\end{align*}$$
(ii) Calculate $[\text{H}_3\text{O}^+]$ in the flask after the NaOH(aq) has been added.

\[
\text{mol}_{\text{HOCl}} = 20.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.175 \text{ mol NaOH}}{1 \text{ L}} = 3.50 \times 10^{-3} \text{ mol}
\]

OH\(^-\)(aq) is the limiting reactant, therefore all of it reacts

\[
\text{HOCl(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{OCl}^-\text{(aq)} + \text{H}_2\text{O(l)}
\]

\[
\begin{array}{c|c|c|c|c}
\text{I} & \text{0.00350} & \text{0.00285} & 0 & - \\
\text{C} & -0.00285 & +0.00285 & +0.00285 & - \\
\text{E} & 0.00065 & 0 & 0.00285 & - \\
\end{array}
\]

\[
M_{\text{HOCl}} = \frac{0.00065 \text{ mol}}{0.02655 \text{ L}} = 0.0245 \text{ M}
\]

\[
M_{\text{OCl}^-} = \frac{0.00285 \text{ mol}}{0.02655 \text{ L}} = 0.107 \text{ M}
\]

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

\[
\begin{array}{c|c|c|c|c|c}
\text{I} & 0.0245 & - & \sim0 & 0.107 \\
\text{C} & -x & - & +x & +x \\
\text{E} & 0.0245 - x & - & +x & 0.107 +x \\
\end{array}
\]

\[K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(0.107 + x)}{(0.0245 - x)}\]

Assume that $0.107 + x \approx 0.107$ and that $0.0245 - x \approx 0.0245$

\[3.2 \times 10^{-8} = \frac{(x)(0.107)}{(0.0245)}\]

\[x = [\text{H}_3\text{O}^+] = 7.3 \times 10^{-9} \text{ M}\]

One point is earned for calculating the initial number of moles of HOCl.

One point is earned for the concentration or number of moles of HOCl and OCl\(^-\) after the neutralization reaction.

One point is earned for the correct $[\text{H}_3\text{O}^+]$.

(iii) Calculate $[\text{OH}^-]$ in the flask after the NaOH(aq) has been added.

\[
[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} = K_w
\]

\[
[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{7.3 \times 10^{-9}} = 1.4 \times 10^{-6} \text{ M}
\]

One point is earned for the correct concentration of $\text{OH}^-$. 
Propanoic acid, HC$_3$H$_5$O$_2$, ionizes in water according to the equation above.

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

$$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]}$$

Notes: Correct expression without $K_a$ earns 1 point.
Entering the value of $K_a$ is acceptable.
Charges must be correct to earn 1 point.

One point is earned for the correct equilibrium expression.

(b) Calculate the pH of a 0.265 M solution of propanoic acid.

$$K_a = 1.34 \times 10^{-5}$$

Assume that $0.265 - x \approx 0.265$,

then $1.34 \times 10^{-5} = \frac{x^2}{0.265}$

$(1.34 \times 10^{-5})(0.265) = x^2$

$3.55 \times 10^{-6} = x^2$

$x = [H^+] = 1.88 \times 10^{-3}$ M

$pH = -\log [H^+] = -\log (1.88 \times 10^{-3}) = 2.725$

One point is earned for recognizing that $[H^+]$ and $[C_3H_5O_2^-]$ have the same value in the equilibrium expression.

One point is earned for calculating $[H^+]$.

One point is earned for calculating the correct pH.
(c) A 0.496 g sample of sodium propanoate, NaC₃H₅O₂, 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, C₃H₅O₂⁻(aq) in the solution

\[
\text{mol NaC}_3\text{H}_5\text{O}_2 = 0.496 \text{ g NaC}_3\text{H}_5\text{O}_2 \times \frac{1 \text{ mol NaC}_3\text{H}_5\text{O}_2}{96.0 \text{ g NaC}_3\text{H}_5\text{O}_2}
\]

\[
\text{mol NaC}_3\text{H}_5\text{O}_2 = 5.17 \times 10^{-3} \text{ mol NaC}_3\text{H}_5\text{O}_2 = \text{mol C}_3\text{H}_5\text{O}_2^{-}
\]

\[
[C_3H_5O_2^-] = \frac{\text{mol C}_3\text{H}_5\text{O}_2^-}{\text{volume of solution}} = \frac{5.17 \times 10^{-3} \text{ mol C}_3\text{H}_5\text{O}_2^-}{0.050 \text{ L}} = 0.103 \text{ M}
\]

One point is earned for calculating the number of moles of NaC₃H₅O₂.
One point is earned for the molarity of the solution.

(ii) The concentration of the H⁺(aq) ion in the solution

\[
\text{HC}_3\text{H}_5\text{O}_2(aq) \Leftrightarrow C_3\text{H}_5\text{O}_2^-(aq) + H^+(aq)
\]

<table>
<thead>
<tr>
<th>L</th>
<th>0.265</th>
<th>0.103</th>
<th>0</th>
<th>0</th>
<th>0.265 - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td>+x</td>
<td>+x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[H^+][C_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(0.103 + x)}{(0.265 - x)}
\]

Assume that: 0.103 + x ≈ 0.103 and 0.265 - x ≈ 0.265

\[
K_a = 1.34 \times 10^{-5} = \frac{(x)(0.103)}{0.265}
\]

\[
x = [H^+] = (1.34 \times 10^{-5}) \times \frac{0.265}{0.103} = 3.45 \times 10^{-5} \text{ M}
\]

The methanoate ion, HCO₂⁻(aq), reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.

\[
\text{HCO}_2^-(aq) + \text{H}_2\text{O}(l) \Leftrightarrow \text{HCO}_2\text{H}(aq) + \text{OH}^-(aq)
\]

(d) Given that [OH⁻] is 4.18 \times 10^{-6} M in a 0.309 M solution of sodium methanoate, calculate each of the following.
(i) The value of $K_b$ for the methanoate ion, HCO$_2$ (aq)

\[
\begin{align*}
\text{HCO}_2 \text{(aq) + H}_2\text{O(l)} \rightleftharpoons \text{HCO}_2\text{H} + \text{OH}^-(aq) \\
\\text{I} & \quad 0.309 & - & 0 & -0 \\
\\text{C} & \quad -x & - & +x & +x \\
\\text{E} & \quad 0.309 - x & - & +x & +x \\
\end{align*}
\]

\[
x = [\text{OH}^-] = 4.18 \times 10^{-6} \text{ M}
\]

\[
K_b = \frac{[\text{OH}^-][\text{HCO}_2\text{H}]}{[\text{HCO}_2^-]} = \frac{(x)(x)}{(0.309 - x)} = \frac{(4.18 \times 10^{-6})^2}{(0.309 - x)}
\]

$x$ is very small ($4.18 \times 10^{-6}$ M), therefore $0.309 - x \approx 0.309$

\[
K_b = \frac{(4.18 \times 10^{-6})^2}{0.309} = 5.65 \times 10^{-11}
\]

One point is earned for substituting $4.18 \times 10^{-6}$ for both $[\text{OH}^-]$ and $[\text{HCO}_2\text{H}]$, and for calculating the value of $K_b$.

(ii) The value of $K_a$ for methanoic acid, HCO$_2$H

\[
K_w = K_a \times K_b
\]

\[
K_w = 1.00 \times 10^{-14}
\]

\[
K_a = K_w \div K_b = \frac{1.00 \times 10^{-14}}{5.65 \times 10^{-11}}
\]

\[
K_a = 1.77 \times 10^{-4}
\]

One point is earned for calculating a value of $K_a$ from the value of $K_b$ determined in part (d)(i).

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

$K_a$ for propanoic acid is $1.34 \times 10^{-5}$, and $K_a$ for methanoic acid is $1.77 \times 10^{-4}$. For acids, the larger the value of $K_a$, the greater the strength; therefore methanoic acid is the stronger acid because $1.77 \times 10^{-4} > 1.34 \times 10^{-5}$.

One point is earned for the correct choice and explanation based on the $K_a$ calculated for methanoic acid in part (d)(ii).
Question 1

\[ C_6H_5COOH(s) \rightleftharpoons C_6H_5COO^- (aq) + H^+(aq) \quad K_a = 6.46 \times 10^{-5} \]

1. Benzoic acid, \( C_6H_5COOH \), 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) \([H^+]\) in the solution

\[
[H^+] = 10^{-4.37} M = 4.3 \times 10^{-5} M
\]

One point is earned for the correct answer.

(ii) \([OH^-]\) in the solution

\[
[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14} M^2}{4.3 \times 10^{-5} M} = 2.3 \times 10^{-10} M
\]

One point is earned for the correct answer.

(iii) The number of moles of \( \text{NaOH} \) 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 \( C_6H_5COO^- (aq) \) in the solution

\[
\text{mol OH}^- \text{ added} = \text{mol } C_6H_5COO^- (aq) \text{ generated, thus mol } C_6H_5COO^- (aq) \text{ in solution} = 2.25 \times 10^{-3} \text{ mol}
\]

One point is earned for the correct answer.

(v) The number of moles of \( C_6H_5COOH \) in the solution

\[
K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} \quad \Rightarrow \quad [C_6H_5COOH] = \frac{[H^+][C_6H_5COO^-]}{K_a}
\]

\[
[C_6H_5COOH] = \frac{(4.3 \times 10^{-5} M) \times 2.25 \times 10^{-3} \text{ mol}}{6.46 \times 10^{-5}} = 3.7 \times 10^{-2} M
\]

\[
\text{thus, mol } C_6H_5COOH = (0.040 \text{ L})(3.7 \times 10^{-2} M) = 1.5 \times 10^{-3} \text{ mol}
\]

One point is earned for the correct molarity.

One point is earned for the correct answer.
Alternative solution for part (a)(v):

\[
\text{pH} = \text{p}K_a + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]} \\
\Rightarrow \text{pH} - \text{p}K_a = \log \frac{[C_6H_5COO^-] - \log [C_6H_5COOH]}{[C_6H_5COOH]} \\
\Rightarrow \log [C_6H_5COOH] = \log \left( \frac{2.25 \times 10^{-3}}{0.040} \right) - (4.37 - 4.190) \\
= -1.25 - 0.18 = -1.43 \\
\Rightarrow [C_6H_5COOH] = 10^{-1.43} = 3.7 \times 10^{-2} \text{M} \\
\text{thus, mol } C_6H_5COOH = (0.040 \text{ L})(3.7 \times 10^{-2} \text{ M}) = 1.5 \times 10^{-3} \text{ mol}
\]

(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

At the equivalence point the solution is basic due to the presence of \( C_6H_5COO^- \) (the conjugate base of the weak acid) that hydrolyzes to produce a basic solution as represented below.

\[
C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^- 
\]

One point is earned for the prediction and the explanation.

In a different titration, a 0.7529 g sample of a mixture of solid \( C_6H_5COOH \) 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

\[
\text{mol } C_6H_5COOH = (0.02478 \text{ L}) \times (0.150 \text{ mol OH}^- \text{L}^{-1}) \times \frac{1 \text{ mol } C_6H_5COOH}{1 \text{ mol OH}^-} \\
= 3.72 \times 10^{-3} \text{ mol } C_6H_5COOH \\
\text{mass } C_6H_5COOH = 3.72 \times 10^{-3} \text{ mol } C_6H_5COOH \times \frac{122 \text{ g } C_6H_5COOH}{1 \text{ mol } C_6H_5COOH} \\
= 0.453 \text{ g } C_6H_5COOH
\]
(ii) The mass percentage of benzoic acid in the solid sample

<table>
<thead>
<tr>
<th>mass % ( \text{C}_6\text{H}_5\text{COOH} )</th>
<th>$\frac{0.453 \text{ g C}_6\text{H}_5\text{COOH}}{0.7529 \text{ g}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$= 60.2%$</td>
</tr>
</tbody>
</table>

One point is earned for the correct answer.
Question 5

Answer the following questions about laboratory solutions involving acids, bases, and buffer solutions.

(a) Lactic acid, \( \text{HC}_3\text{H}_5\text{O}_3 \), reacts with water to produce an acidic solution. Shown below are the complete Lewis structures of the reactants.

\[
\begin{align*}
\text{H} & \quad :\text{O} : \quad :\text{O} : \\
\text{H} & \quad \text{--C--C--C--O--H} + \quad \text{H} \quad \text{O--H} \\
\text{H} & \quad :\text{O} : \quad :\text{O} \\
\text{H} & \quad \text{--C--C--C--O--H} \\
\end{align*}
\]

In the space provided above, complete the equation by drawing the complete Lewis structures of the reaction products.

(b) Choosing from the chemicals and equipment listed below, describe how to prepare 100.00 mL of a 1.00 \( M \) aqueous solution of \( \text{NH}_4\text{Cl} \) (molar mass 53.5 g mol\(^{-1}\)). Include specific amounts and equipment where appropriate.

\[
\begin{align*}
\text{NH}_4\text{Cl}(s) & \quad 50 \text{ mL buret} & \quad 100 \text{ mL graduated cylinder} & \quad 100 \text{ mL pipet} \\
\text{Distilled water} & \quad 100 \text{ mL beaker} & \quad 100 \text{ mL volumetric flask} & \quad \text{Balance} \\
\end{align*}
\]

mass of \( \text{NH}_4\text{Cl} \) = (0.100 L)(1.00 mol L\(^{-1}\))(53.5 g mol\(^{-1}\)) = 5.35 g \( \text{NH}_4\text{Cl} \)

1. Measure out 5.35 g \( \text{NH}_4\text{Cl} \) using the balance.
2. Use the 100 mL graduated cylinder to transfer approximately 25 mL of distilled water to the 100 mL volumetric flask.
3. Transfer the 5.35 g \( \text{NH}_4\text{Cl} \) to the 100 mL volumetric flask.
4. Continue to add distilled water to the volumetric flask while swirling the flask to dissolve the \( \text{NH}_4\text{Cl} \) and remove all \( \text{NH}_4\text{Cl} \) particles adhered to the walls.
5. Carefully add distilled water to the 100 mL volumetric flask until the bottom of the meniscus of the solution reaches the etched mark on the flask.

One point is earned for each correct structure.

One point is earned for the mass.

One point is earned for using a volumetric flask.

One point is earned for diluting to the mark.
Question 5 (continued)

(c) Two buffer solutions, each containing acetic acid and sodium acetate, are prepared. A student adds 0.10 mol of HCl to 1.0 L of each of these buffer solutions and to 1.0 L of distilled water. The table below shows the pH measurements made before and after the 0.10 mol of HCl is added.

<table>
<thead>
<tr>
<th></th>
<th>pH Before HCl Added</th>
<th>pH After HCl Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>7.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Buffer 1</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Buffer 2</td>
<td>4.7</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(i) Write the balanced net-ionic equation for the reaction that takes place when the HCl is added to buffer 1 or buffer 2.

\[
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}
\]

One point is earned for the equation.

(ii) Explain why the pH of buffer 1 is different from the pH of buffer 2 after 0.10 mol of HCl is added.

Before the HCl was added, each buffer had the same pH and thus had the same [H\(^+\)]. Because \( K_a \) for acetic acid is a constant, the ratio of [H\(^+\)] to \( K_a \) must also be constant; this means that the ratio of [HC\(_2\)H\(_3\)O\(_2\)] to [C\(_2\)H\(_3\)O\(_2\)\(^-\)] is the same for both buffers, as shown by the following equation, derived from the equilibrium-constant expression for the dissociation of acetic acid.

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

After the addition of the H\(^+\), the ratio in buffer 1 must have been greater than the corresponding ratio in buffer 2, as evidenced by their respective pH values. Thus a greater proportion of the C\(_2\)H\(_3\)O\(_2\)\(^-\) in buffer 1 must have reacted with the added H\(^+\) compared to the proportion that reacted in buffer 2. The difference between these proportions means that the original concentrations of HC\(_2\)H\(_3\)O\(_2\) and C\(_2\)H\(_3\)O\(_2\)\(^-\) had to be smaller in buffer 1 than in buffer 2.

One point is earned for a correct answer involving better buffering capacity or relative amount of base (acetate ion).
(iii) Explain why the pH of buffer 1 is the same as the pH of buffer 2 before 0.10 mol of HCl is added.

Both buffer solutions have the same acid to conjugate-base mole ratio in the formula below.

\[
[H^+] = K_a \left( \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} \right)
\]

Therefore, the buffers have the same [H\(^+\)] and pH.

One point is earned for the correct answer involving ratio of acid to base in the buffer.
Question 1

HF(aq) + H₂O(l) ⇌ H₃O⁺(aq) + F⁻(aq)  \quad K_a = 7.2 \times 10^{-4}

Hydrofluoric acid, HF(aq), dissociates in water as represented by the equation above.

(a) Write the equilibrium-constant expression for the dissociation of HF(aq) in water.

\[
K_a = \frac{[H_3O^+][F^-]}{[HF]} \quad \text{One point is earned for the correct expression.}
\]

(b) Calculate the molar concentration of H₃O⁺ in a 0.40 M HF(aq) solution.

\[
K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{0.40-x} = 7.2 \times 10^{-4}
\]

Assume \( x << 0.40 \), then \( x^2 = (0.40)(7.2 \times 10^{-4}) \)

\[
x = [H_3O^+] = 0.017 \, M
\]

One point is earned for the correct setup (or the setup consistent with part (a)).

One point is earned for the correct concentration.

HF(aq) reacts with NaOH(aq) according to the reaction represented below.

\[
\text{HF}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{F}^-(aq)
\]

A volume of 15 mL of 0.40 M NaOH(aq) is added to 25 mL of 0.40 M HF(aq) solution. Assume that volumes are additive.

(c) Calculate the number of moles of HF(aq) remaining in the solution.

\[
\text{mol HF(aq)} = \text{initial mol HF(aq)} - \text{mol NaOH(aq) added}
\]

\[
= (0.025 \, \text{L})(0.40 \, \text{mol L}^{-1}) - (0.015 \, \text{L})(0.40 \, \text{mol L}^{-1})
\]

\[
= 0.010 \, \text{mol} - 0.0060 \, \text{mol} = 0.004 \, \text{mol}
\]

One point is earned for determining the initial number of moles of HF and OH⁻.

One point is earned for setting up and doing correct subtraction.

(d) Calculate the molar concentration of F⁻(aq) in the solution.

\[
\frac{\text{mol F}^-(aq) \text{ formed}}{\text{mol NaOH(aq) added}} = \frac{0.0060 \, \text{mol F}^-(aq)}{0.0060 \, \text{mol}} = 0.15 \, M \, \text{F}^-(aq)
\]

One point is earned for determining the number of moles of F⁻(aq).

One point is earned for dividing the number of moles of F⁻(aq) by the correct total volume.
(e) Calculate the pH of the solution.

\[
[\text{HF}] = \frac{0.004 \text{ mol HF}}{0.040 \text{ L}} = 0.10 \text{ M HF}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \Rightarrow \frac{[\text{HF}] \times K_a}{[\text{F}^-]} = [\text{H}_3\text{O}^+]
\]

\[
\Rightarrow \frac{0.10 \text{ M} \times (7.2 \times 10^{-4})}{0.15 \text{ M}} = 4.8 \times 10^{-4}
\]

\[
\Rightarrow \text{pH} = -\log (4.8 \times 10^{-4}) = 3.32
\]

OR

\[
\text{pH} = pK_a + \log \frac{[\text{F}^-]}{[\text{HF}]}
\]

\[
= -\log (7.2 \times 10^{-4}) + \log \frac{0.15 \text{ M}}{0.10 \text{ M}}
\]

\[
= 3.14 + 0.18
\]

= 3.32

One point is earned for indicating that the resulting solution is a buffer (e.g., by showing a ratio of \([\text{F}^-]\) to \([\text{HF}]\) or moles of \(\text{F}^-\) to \(\text{HF}\)).

One point is earned for the correct calculation of pH.
Question 1 (10 points)

A pure 14.85 g sample of the weak base ethylamine, C₂H₅NH₂, is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the C₂H₅NH₂ in the solution.

\[
n_{C_2H_5NH_2} = \frac{14.85 \text{ g C}_2\text{H}_5\text{NH}_2 \times 1 \text{ mol C}_2\text{H}_5\text{NH}_2}{45.09 \text{ g C}_2\text{H}_5\text{NH}_2} = 0.3293 \text{ mol C}_2\text{H}_5\text{NH}_2
\]

\[
M_{C_2H_5NH_2} = \frac{0.3293 \text{ mol C}_2\text{H}_5\text{NH}_2}{0.500 \text{ L}} = 0.659 M
\]

The aqueous ethylamine reacts with water according to the equation below.

\[
\text{C}_2\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{C}_2\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)
\]

(b) Write the equilibrium-constant expression for the reaction between C₂H₅NH₂(aq) and water.

\[
K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} \quad \text{One point is earned for the correct expression.}
\]

(c) Of C₂H₅NH₂(aq) and C₂H₅NH₃⁺(aq), which is present in the solution at the higher concentration at equilibrium? Justify your answer.

C₂H₅NH₂ is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small \( K_b \) value. Therefore only partial dissociation of C₂H₅NH₂ occurs in water, and \([\text{C}_2\text{H}_5\text{NH}_3^+]\) is thus less than \([\text{C}_2\text{H}_5\text{NH}_2]\).
(d) A different solution is made by mixing 500. mL of 0.500 M C₂H₅NH₂ with 500. mL of 0.200 M HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

(i) Calculate the concentration of OH⁻(aq) in the solution.

\[
\text{pH} = -\log[\text{H}^+] \\
[\text{H}^+] = 10^{-10.93} = 1.17 \times 10^{-11} \\
[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.00 \times 10^{-14}}{1.17 \times 10^{-11}} = 8.5 \times 10^{-4} \text{ M}
\]

OR

\[
\text{pOH} = 14 - \text{pH} = 14 - 10.93 = 3.07 \\
\text{pOH} = -\log[\text{OH}^-] \\
[\text{OH}^-] = 10^{-3.07} = 8.5 \times 10^{-4} \text{ M}
\]

One point is earned for the correct concentration.

(ii) Write the net-ionic equation that represents the reaction that occurs when the C₂H₅NH₂ solution is mixed with the HCl solution.

\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O}
\]

One point is earned for the correct equation.

(iii) Calculate the molar concentration of the C₂H₅NH₃⁺(aq) that is formed in the reaction.

\[
\text{moles of C}_2\text{H}_5\text{NH}_2 = 0.500 \text{ L} \times \frac{0.500 \text{ mol}}{1.00 \text{ L}} = 0.250 \text{ mol} \\
\text{moles of } \text{H}_3\text{O}^+ = 0.500 \text{ L} \times \frac{0.200 \text{ mol}}{1.00 \text{ L}} = 0.100 \text{ mol}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
& [\text{C}_2\text{H}_5\text{NH}_2] & [\text{H}_3\text{O}^+] & [\text{C}_2\text{H}_5\text{NH}_3^+] \\
\hline\text{initial value} & 0.250 & 0.100 & \sim 0 \\
\hline\text{change} & -0.100 & -0.100 & +0.100 \\
\hline\text{final value} & 0.150 & \sim 0 & 0.100 \\
\hline
\end{array}
\]

\[
[\text{C}_2\text{H}_5\text{NH}_3^+] = \frac{0.100 \text{ mol C}_2\text{H}_5\text{NH}_3^+}{1.00 \text{ L}} = 0.100 \text{ M}
\]

One point is earned for the correct concentration.
(iv) Calculate the value of $K_b$ for $C_2H_5NH_2$.

\[
[C_2H_5NH_2] = \frac{0.150 \text{ mol} \ C_2H_5NH_2}{1.00 \text{ L}} = 0.150 \text{ M}
\]

\[
K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(0.100)(8.5 \times 10^{-4})}{0.150} = 5.67 \times 10^{-4}
\]

One point is earned for the correct calculation of the molarity of $C_2H_5NH_2$ after neutralization.

One point is earned for the correct value.
Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$ at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>HOBr</td>
<td>$2.4 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

(i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of $K_a$.

| HOCl is the stronger acid because its $K_a$ value is greater than the $K_a$ value of HOBr. | One point is earned for the correct answer with justification. |

(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

| [H: :Cl] | One point is earned for a correct diagram. |

(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

| HOI is a weaker acid than HOCl because the O–H bond in HOI is stronger than the O–H bond in HOCl. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in HOCl. OR The conjugate base OCl$^-$ is more stable than OI$^-$ because Cl, being more electronegative, is better able to accommodate the negative charge. | One point is earned for predicting that HOI is a weaker acid than HOCl and stating that iodine has a lower electronegativity than chlorine and EITHER stating that this results in a stronger O–H bond in HOI OR stating that this decreases the stability of the OI$^-$ ion in solution. |
(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

\[
\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{OCl}^- + \text{H}_3\text{O}^+
\]

**OR**

\[
\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+
\]

One point is earned for the correct equation.

(c) A 1.2 \text{ M} \text{ NaOCl} solution is prepared by dissolving solid \text{ NaOCl} in distilled water at 298 K. The hydrolysis reaction \( \text{OCl}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^+(aq) \) occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between \( \text{OCl}^-(aq) \) and \( \text{H}_2\text{O}(l) \).

\[
K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}\]

One point is earned for the correct expression.

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7}
\]

One point is earned for the correct value with supporting work.

(iii) Calculate the value of \([\text{OH}^-]\) in the 1.2 \text{ M} \text{ NaOCl} solution at 298 K.

\[
\begin{array}{|c|c|c|c|}
\hline
 & [\text{OCl}^-] & [\text{HOCl}] & [\text{OH}^-] \\
\hline
\text{initial value} & 1.2 & 0 & \approx 0 \\
\hline
\text{change} & -x & x & x \\
\hline
\text{equilibrium value} & 1.2 - x & x & x \\
\hline
\end{array}
\]

One point is earned for the correct setup.

One point is earned for the correct answer with supporting calculations.

\[
K_{\text{hyd}} = 3.4 \times 10^{-7} = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{(x)(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}
\]

\[
(1.2)(3.4 \times 10^{-7}) = x^2 \Rightarrow
\]

\[
x^2 = [\text{OH}^-] = 6.4 \times 10^{-4}\text{ M}
\]
(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

(i) Calculate the value of $[H_3O^+]$ in the buffer solution.

\[
[H^+] = 10^{-6.48} = 3.3 \times 10^{-7} \text{M}
\]

One point is earned for the correct value.

(ii) Indicate which of HOCl(\textit{aq}) or OCl(\textit{aq}) is present at the higher concentration in the buffer solution. Support your answer with a calculation.

\[
\begin{align*}
[H^+] &= 3.3 \times 10^{-7} \text{M} \text{ and } K_a \text{ for HOCl} = 2.9 \times 10^{-8} \\
K_a &= \frac{[H^+][\text{OCl}^-]}{[\text{HOCl}]} \\
2.9 \times 10^{-8} &= \frac{(3.3 \times 10^{-7})[\text{OCl}^-]}{[\text{HOCl}]} \\
\frac{[\text{OCl}^-]}{[\text{HOCl}]} &= \frac{2.9 \times 10^{-8}}{3.3 \times 10^{-7}} = 0.088 \implies [\text{HOCl}] > [\text{OCl}^-]
\end{align*}
\]

One point is earned for the correct answer with supporting buffer calculations.
A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

(a) Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH solution.

\[
M_1V_1 = M_2V_2
\]

\[
V_1 = \frac{M_2V_2}{M_1} = \frac{(1.250 \text{ M})(100.0 \text{ mL})}{5.000 \text{ M}} = 25.00 \text{ mL}
\]

1 point is earned for the correct volume.

(b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH solution using 5.000 M NaOH and equipment selected from the list below.

<table>
<thead>
<tr>
<th>Balance</th>
<th>25 mL Erlenmeyer flask</th>
<th>100 mL graduated cylinder</th>
<th>100 mL volumetric flask</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mL buret</td>
<td>100 mL Florence flask</td>
<td>25 mL pipet</td>
<td>100 mL beaker</td>
</tr>
<tr>
<td>Eyedropper</td>
<td>Drying oven</td>
<td>Wash bottle of distilled H\text{₂}O</td>
<td>Crucible</td>
</tr>
</tbody>
</table>

Pipet 25.00 mL of 5.000 M NaOH solution into the 100 mL volumetric flask.
Fill the volumetric flask to the calibration line with distilled water; using an eyedropper for the last few drops is advised.
Cap the volumetric flask and invert several times to ensure homogeneity.

1 point is earned for descriptions of any two of the three steps.
An additional point is earned if all three steps are described.

(c) The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

(i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

When a weak acid is titrated with a strong base, the reaction forms water and the A⁻ ion.

\[
HA + OH^- \rightleftharpoons A^- + H_2O
\]

The A⁻ ion formed in the titration reacts with the solvent water to release OH⁻ ions, making the solution basic at the equivalence point.

\[
A^- + H_2O \rightleftharpoons HA + OH^-\]

1 point is earned for either the correct equation or a clear statement that the conjugate base, A⁻, is a (weak) base.

1 point is earned for indicating that the solution is basic because of the formation of OH⁻.
(ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl red</td>
<td>5</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>7</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>9</td>
</tr>
</tbody>
</table>

Because the pH is basic at the equivalence point, it is best to use an indicator that changes color in basic solution. Therefore, phenolphthalein would be the best indicator for the titration.

1 point is earned for an answer consistent with the answer to part (c)(i) with justification.

(d) The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.

(i) What is the value of the acid-dissociation constant, Kₐ, for the weak acid? Explain your reasoning.

The resulting solution is at the half-equivalence-point, where [HA] = [A⁻], thus pH = pKₐ = 5.0 ⇒ Kₐ = 1 × 10⁻⁵.

1 point is earned for showing that the system is at the half-equivalence point.
1 point is earned for the correct value of Kₐ.

(ii) Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

The resulting solution is a buffer; therefore adding a few drops of acid or base does not appreciably change the pH.

1 point is earned for indicating that the solution is a buffer.
1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH₃, or NH₄Cl, as shown above. Each solution is at 25°C.

(a) Determine the pH of the solution in beaker 1. Justify your answer.

\[ \text{pH} = -\log[H^+] = -\log(0.100) = 1.000 \]

1 point is earned for the correct pH.

(b) In beaker 2, the reaction \( \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \) occurs. The value of \( K_b \) for \( \text{NH}_3(aq) \) is \( 1.8 \times 10^{-5} \) at 25°C.

(i) Write the \( K_b \) expression for the reaction of \( \text{NH}_3(aq) \) with \( \text{H}_2\text{O}(l) \).

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

1 point is earned for the correct expression.

(ii) Calculate the \([\text{OH}^-]\) in the solution in beaker 2.

Let \([\text{OH}^-] = x\), then \( K_b = \frac{(x)(x)}{(0.100 - x)} \)

Assume that \( x \ll 0.100 \text{ M} \), then

\[ 1.8 \times 10^{-5} = \frac{x^2}{0.100} \Rightarrow x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M} \]

1 point is earned for the correct setup.
1 point is earned for the correct answer.

(c) In beaker 3, the reaction \( \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \) occurs.

(i) Calculate the value of \( K_a \) for \( \text{NH}_4^+(aq) \) at 25°C.

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \]

1 point is earned for the correct answer.
Question 1 (continued)

(ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

In the resulting solution, \([\text{NH}_3] = [\text{NH}_4^+]\):

\[
K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_4^+][\text{H}_3\text{O}^+]}{[\text{NH}_3]}
\]

Thus \([\text{H}_3\text{O}^+] = 5.6 \times 10^{-10} \), \(\text{pH} = -\log(5.6 \times 10^{-10}) = 9.25\)

1 point is earned for noting that the solution is a buffer with \([\text{NH}_3] = [\text{NH}_4^+]\).

1 point is earned for the correct pH.

(d) The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

(i) Is the resulting solution an effective buffer? Justify your answer.

The resulting solution is not an effective buffer. Virtually all of the \(\text{NH}_3\) in the solution formed in (c)(ii) will react with the \(\text{H}_3\text{O}^+\) from solution 1:

\[
\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}
\]

leaving mostly \(\text{NH}_4^+\) in the final solution. Since only one member of the \(\text{NH}_4^+ / \text{NH}_3\) conjugate acid-base pair is left, the solution cannot buffer both base and acid.

1 point is earned for the correct response with an acceptable justification.

(ii) Calculate the final \([\text{NH}_4^+]\) in the resulting solution at 25°C.

\[
\text{moles} = (\text{volume})(\text{molarity})
\]

moles \(\text{H}_3\text{O}^+\) in sol. 1 = \((0.0250)(0.100) = 0.00250 \text{ mol}
\]

moles \(\text{NH}_3\) in sol. 2 = \((0.0250)(0.100) = 0.00250 \text{ mol}
\]

moles \(\text{NH}_4^+\) in sol. 3 = \((0.0250)(0.100) = 0.00250 \text{ mol}
\]

When the solutions are mixed, the \(\text{H}_3\text{O}^+\) and \(\text{NH}_3\) react to form \(\text{NH}_4^+\), resulting in a total of 0.00500 mol \(\text{NH}_4^+\). The final volume is the sum (25.0 + 25.0 + 25.0) = 75.0 mL.

The final concentration of \(\text{NH}_4^+\) = \((0.00500 \text{ mol}/0.0750 \text{ L}) = 0.0667 \text{ M.}\n
1 point is earned for the correct calculation of moles of \(\text{NH}_4^+\).
1 point is earned for the correct calculation of the final volume and concentration.
A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

<table>
<thead>
<tr>
<th>Volume of 0.250 M NaOH Added (mL)</th>
<th>pH of Titrated Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>?</td>
</tr>
<tr>
<td>10.0</td>
<td>3.72</td>
</tr>
<tr>
<td>20.0</td>
<td>4.20</td>
</tr>
<tr>
<td>30.0</td>
<td>?</td>
</tr>
<tr>
<td>40.0</td>
<td>8.62</td>
</tr>
<tr>
<td>50.0</td>
<td>12.40</td>
</tr>
</tbody>
</table>

(a) Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.

The pH at the equivalence point is above 7, which indicates that HA is a weak acid.

1 point is earned for the correct explanation.

(b) Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

\[
\text{HA}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

1 point is earned for writing the net-ionic equation balanced for mass and charge.

(c) Calculate the number of moles of HA that were titrated.

At the equivalence point, the number of moles of base added equals the number of moles of acid initially present.

\[
0.0400 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} = 0.0100 \text{ mol HA}
\]

1 point is earned for the correct number of moles.
(d) Calculate the molar mass of HA.

\[
M_M = \frac{\text{mass of acid}}{\text{moles of acid}} = \frac{1.22 \text{ g}}{0.0100 \text{ mol}} = 122 \text{ g/mol}
\]

1 point is earned for the correct molar mass.

The equation for the dissociation reaction of HA in water is shown below.

\[
\text{HA(aq) + H}_2\text{O(l) } \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \quad K_a = 6.3 \times 10^{-5}
\]

(e) Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 M. Determine the pH of the initial HA solution.

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]

\[6.3 \times 10^{-5} = \frac{(x)(x)}{(0.200-x)}; \text{ assume that } x \ll 0.200 \text{ M.}
\]

\[x = [\text{H}_3\text{O}^+] = 3.5 \times 10^{-3} \text{ M}
\]

\[\text{pH} = -\log([\text{H}_3\text{O}^+]) = -\log(3.5 \times 10^{-3}) = 2.45
\]

1 point is earned for the appropriate substitution into the \(K_a\) expression.

1 point is earned for the correct \([\text{H}_3\text{O}^+]\).

1 point is earned for the calculation of pH.

(f) Calculate the value of \([\text{H}_3\text{O}^+]\) in the solution after 30.0 mL of NaOH solution is added and the total volume of the solution is 80.0 mL.

\[
\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}
\]

mol before rxn: 0.0100 0.00750 0.00000

mol after rxn: 0.00250 0.00000 0.00750

\[\text{mol of A}^-: \frac{0.00250\text{mol}}{0.0800\text{L}} = 3.13 \times 10^{-2} \text{ M}
\]

\[\text{mol of HA: } \frac{0.00750\text{mol}}{0.0800\text{L}} = 9.38 \times 10^{-2} \text{ M}
\]

\[K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]

\[6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2} + x)}{(3.13 \times 10^{-2} - x)}
\]

Assume that \(x \ll 9.38 \times 10^{-2} \text{ M} \) and \(3.13 \times 10^{-2} \text{ M}\

then \(6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2})}{(3.13 \times 10^{-2})}
\]

\[x = [\text{H}_3\text{O}^+] = 2.10 \times 10^{-5} \text{ M}
\]

1 point is earned for the correct calculation of \([\text{H}_3\text{O}^+]\).

1 point is earned for the appropriate substitution into the equilibrium expression.

1 point is earned for the correct calculation of \([\text{H}_3\text{O}^+]\).