Week 25

AP Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

AP Chemistry Name: ____________ Score: ______

1. A conjugate acid-base pair differs by...
   - ☐ one proton (H^+)
   - ☐ one electron
   - ☐ one neutron
2. Find the pH of a 0.01 M strong acid.

   ____
3. A larger K_a means the weak acid is...
   - ☐ stronger
   - ☐ weaker
   - ☐ more dilute
4. A buffer is made from...
   - ☐ a weak acid and its conjugate base
   - ☐ a strong acid alone
   - ☐ pure water
5. At the equivalence point, the moles of acid and base are...
   - ☐ equal
   - ☐ both zero
   - ☐ doubled
6. A weaker bond to hydrogen makes an acid...
   - ☐ stronger
   - ☐ weaker
   - ☐ neutral
7. A buffer has p$K_a = 5.0$ with equal acid and base. Its pH?

   ____
8. If $[H^+] = 1.0 \times 10^{-4}$, find $[OH^-]$. Enter the exponent (a negative number).

   ____

9. A solution has pH = 9 at 25 degrees. Its pOH?

   ____

10. A weak acid and a dilute acid are the same thing.

   ☐ True ☐ False

AP Chemistry

1. **one proton (H^+)**

   The acid loses one H^+ to become its conjugate base.

2. **2**

   $[H^+] = 10^{-2}$, so $pH = -\log(10^{-2}) = 2$.

3. **stronger**

   A bigger K_a means more ionization – a stronger weak acid.

4. **a weak acid and its conjugate base**

   A buffer pairs a weak acid with its conjugate base.

5. **equal**

   Equivalence means the moles exactly match.

6. **stronger**

   A weaker H bond releases the proton more easily.

7. **5**

   $\log 1 = 0$, so $pH = pK_a = 5.0$.

8. **-10**

   $[OH^-] = 10^{-14}/10^{-4} = 10^{-10}$.

9. **5**

   $pOH = 14 - pH = 14 - 9 = 5$.

10. **False**

    Weak is about ionization; dilute is about concentration.

8.1 Introduction to Acids and Bases

Name: __________ Class: ________ Date: _________ **Total: 10 marks**

KEY WORDS acid 酸 • base 碱 • weak 弱 • weak acid 弱酸 • strong 强

Objective

Build the skills to answer exam questions on **acids and bases** — the basic definitions.

You must be able to:

- use the **Brønsted-Lowry** definitions (proton donor / acceptor)
- distinguish **strong** 强 from **weak** 弱 acids and bases
- write the ionization of an acid in water

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Brønsted-Lowry

An **acid** donates H^+; a **base** accepts H^+. In water an acid produces H_3O^+ (hydronium); a base produces OH^-.

■ Strong vs weak

- A **strong** acid/base ionizes **completely** (HCl, NaOH) — a single arrow.
- A **weak** acid/base ionizes **partially** (CH_3COOH, NH_3) — an equilibrium arrow.

■ A worked ionization

Strong: $HCl \rightarrow H^+ + Cl^-$ (complete). Weak: $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ (partial, so a small K_a).

■ Recognising strong acids

The common strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$. Assume other acids are weak.

2 Practice

Now apply the methods above.

2.1 Define a Brønsted-Lowry base. [1]

2.2 Write the ionization of the strong acid HNO_3 in water. [1]

2.3 Why is a weak acid written with an equilibrium arrow? [1]

3 Exam-style questions

3.1 A strong acid in water [1]

- **A** ionizes completely
- **B** ionizes partially
- **C** does not ionize
- **D** forms OH^-

3.2 Compare HCl and CH_3COOH (acetic acid) at the same concentration.

(a) Which ionizes more? [1]

(b) Which has the higher $[H^+]$? Explain. [2]

3.3 Write the equilibrium for the weak base ammonia NH_3 reacting with water. [3]

Solutions

2.1 A proton (H^+) acceptor.

2.2 $HNO_3 \rightarrow H^+ + NO_3^-$.

2.3 It only ionizes partially, so an equilibrium exists between the molecule and its ions.

3.1 **A** — ionizes completely.

3.2 (a) HCl. (b) HCl — it is strong and ionizes completely, giving a higher $[H^+]$ than the partially-ionized weak acetic acid.

3.3 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.

Question 3: Version J

The following information applies to all parts.

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3. Nitrous acid, HNO_2, is a weak acid that ionizes according to Equation 1.

$$\text{Equation 1: } HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq) \quad K_a = 5.6\times10^{-4} \text{ at } 298 \text{ K}$$

Part A

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $HNO_2(aq)$ with an initial concentration of $0.125\ M$ has a pH of 2.09.

i. **Calculate** the value of $[H_3O^+]$ in the solution. Show the work that leads to your answer.

ii. **Calculate** $[HNO_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of $0.125\ M\ HNO_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[HNO_2] = 0.114\ M$, $[NO_2^-] = 0.0109\ M$, and $[H_3O^+] = 0.0109\ M$.

i. **Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.

ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

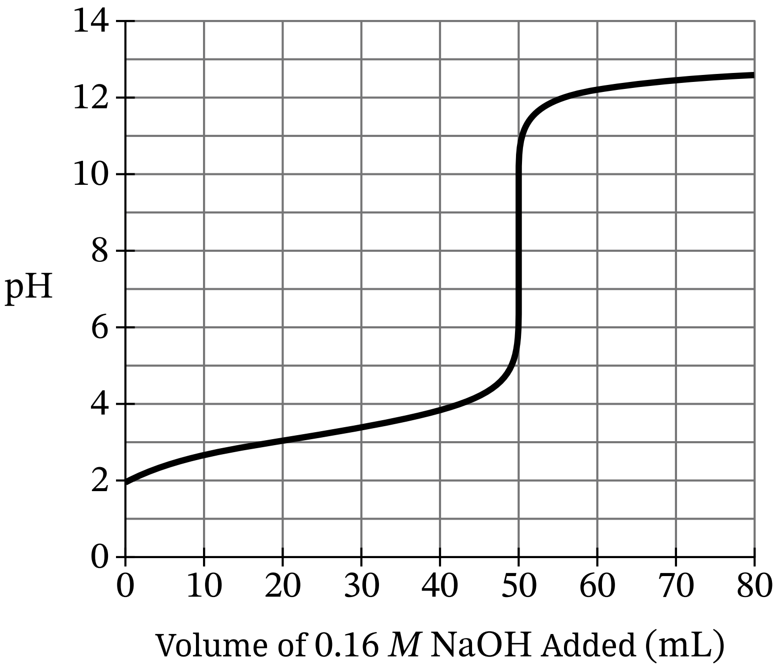
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $HNO_2(aq)$ in the bottle, the student titrates 35.0 mL of the $HNO_2(aq)$ with 0.16 M $NaOH(aq)$ at 298 K, which reacts according to Equation 2.

$$\text{Equation 2: } HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $HNO_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[HNO_2] > [NO_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a; the autoionization of water, K_w; and the neutralization reaction represented by Equation 2, K_2.

Table 1

Chemical Equation	Equilibrium Constant
$HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

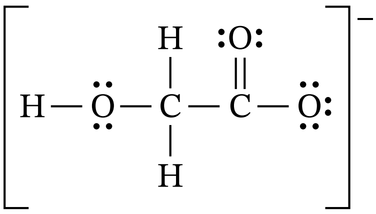
Table 2

Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $HNO_2(aq)$ solution and titrating the solution with 0.16 M $NaOH(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

7. Answer the following questions about the glycolate ion, $C_2H_3O_3^-$, which acts as a base in aqueous solution. A Lewis diagram for the ion is provided.



A. On the Lewis diagram in part A, circle the atom that accepts the proton when the glycolate ion reacts with water.

When the glycolate ion reacts with water, it forms glycolic acid, $HC_2H_3O_3$, according to the following equation. The K_b expression for the reaction is provided.

$$C_2H_3O_3^-(aq) + H_2O(l) \rightleftarrows HC_2H_3O_3(aq) + OH^-(aq) \qquad K_b = \frac{[HC_2H_3O_3][OH^-]}{[C_2H_3O_3^-]}$$

B. At 25°C, a 2.5 M solution of glycolate is found to have $[OH^-] = 1.3 \times 10^{-5}\ M$.

i. Calculate the value of K_b for the glycolate ion.

ii. Using your answer to part B (i), calculate the value of K_a for glycolic acid at 25°C.

Glycolic acid can be produced from the hydrolysis of methyl glycolate, $C_3H_6O_3$. A proposed mechanism for the reaction is given.

Step 1: $C_3H_6O_3 + H_3O^+ \rightleftarrows C_2H_5O_3^+ + CH_3OH$

Step 2: $\underline{C_2H_5O_3^+ + H_2O \rightleftarrows HC_2H_3O_3 + H_3O^+}$

Overall: $C_3H_6O_3 + H_2O \rightleftarrows HC_2H_3O_3 + CH_3OH$

C. A student claims that H_3O^+ is a catalyst for the reaction. Do you agree or disagree? Justify your answer based on the mechanism given.

STOP

END OF EXAM

Compound	Melting Point (°C)
LiI	449
KI	686
LiF	845
NaF	993

6. A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

   (a) Select two compounds from the table and explain how the data support the student's hypothesis.

   (b) Identify a compound from the table that can be dissolved in water to produce a basic solution. Write the net ionic equation for the reaction that occurs to cause the solution to be basic.

AP Chemistry: **2014**

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

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

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

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

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

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

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

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

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

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

AP CHEMISTRY • EXERCISE SHEET

8.2 pH and pOH of Strong Acids and Bases

Name: ______________ Class: __________ Date: ____________ **Total: 12 marks**

KEY WORDS strong base 强碱 • ph pH 值 • acid 酸 • strong acid 强酸 • base 碱

Objective

Build the skills to answer exam questions on **pH and pOH** of strong acids and bases.

You must be able to:

- use $pH = -\log[H^+]$ and $pOH = -\log[OH^-]$
- use $pH + pOH = 14$ and $[H^+][OH^-] = 1 \times 10^{-14}$
- find pH for a strong acid or base of known concentration

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

The definitions

$$pH = -\log[H^+], \qquad pOH = -\log[OH^-].$$

At 25°C, $pH + pOH = 14$ and $[H^+][OH^-] = 1 \times 10^{-14}$.

Strong acid pH

A strong acid ionizes completely, so $[H^+]$ equals its concentration. For 0.010 M HCl: $pH = -\log(0.010) = 2$.

Strong base pH

A strong base gives $[OH^-]$ equal to its concentration. For 0.010 M NaOH: $pOH = 2$, so $pH = 14 - 2 = 12$.

Finding [H+] back from pH

Reverse with $[H^+] = 10^{-pH}$. A pH of 3 means $[H^+] = 1 \times 10^{-3}$ M.

2 Practice

Now apply the methods above.

2.1 Find the pH of 0.001 M HCl. [2]

2.2 Find the pOH of 0.010 M NaOH, then the pH. [2]

2.3 Find $[H^+]$ for a solution of $pH = 4$. [1]

3 Exam-style questions

3.1 At 25°C, $pH + pOH =$ [1]

- **A** 7
- **B** 10
- **C** 14
- **D** 1

3.2 A 0.0050 M solution of HNO_3 (a strong acid).

(a) State $[H^+]$. [1]

(b) Find the pH. [2]

3.3 A 0.020 M solution of NaOH.

(a) Find the pOH. [2]

(b) Find the pH. [1]

Solutions

2.1 pH $= -\log(0.001) = 3$.

2.2 pOH $= -\log(0.010) = 2$; pH $= 14 - 2 = 12$.

2.3 $[H^+] = 10^{-4} = 1 \times 10^{-4}$ M.

3.1 **C** — 14.

3.2 (a) $[H^+] = 0.0050$ M. (b) pH $= -\log(0.0050) = 2.30$.

3.3 (a) pOH $= -\log(0.020) = 1.70$. (b) pH $= 14 - 1.70 = 12.30$.

Question 3: Version J

The following information applies to all parts.

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3. Nitrous acid, HNO_2, is a weak acid that ionizes according to Equation 1.

$$\text{Equation 1: } HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq) \quad K_a = 5.6\times10^{-4} \text{ at } 298 \text{ K}$$

Part A

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $HNO_2(aq)$ with an initial concentration of $0.125\ M$ has a pH of 2.09.

i. **Calculate** the value of $\left[H_3O^+\right]$ in the solution. Show the work that leads to your answer.

ii. **Calculate** $[HNO_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of $0.125\ M$ $HNO_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[HNO_2] = 0.114\ M$, $[NO_2^-] = 0.0109\ M$, and $\left[H_3O^+\right] = 0.0109\ M$.

i. **Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.

ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

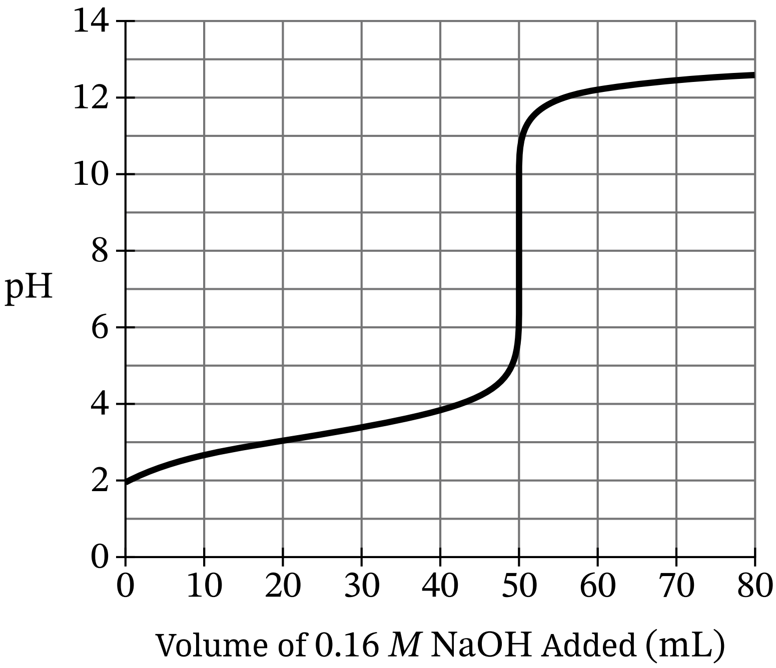
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $HNO_2(aq)$ in the bottle, the student titrates 35.0 mL of the $HNO_2(aq)$ with 0.16 M $NaOH(aq)$ at 298 K, which reacts according to Equation 2.

$$\text{Equation 2: } HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $HNO_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[HNO_2] > [NO_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a; the autoionization of water, K_w; and the neutralization reaction represented by Equation 2, K_2.

Table 1

Chemical Equation	Equilibrium Constant
$HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$	$K_2 = \ ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

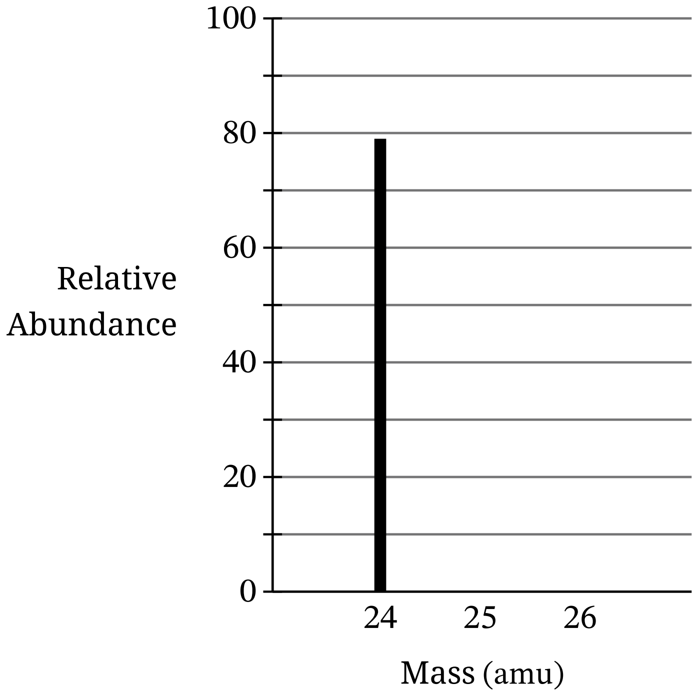
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $HNO_2(aq)$ solution and titrating the solution with 0.16 M $NaOH(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

1. Answer the following questions about magnesium.

A. An incomplete mass spectrum for magnesium is shown in the diagram.

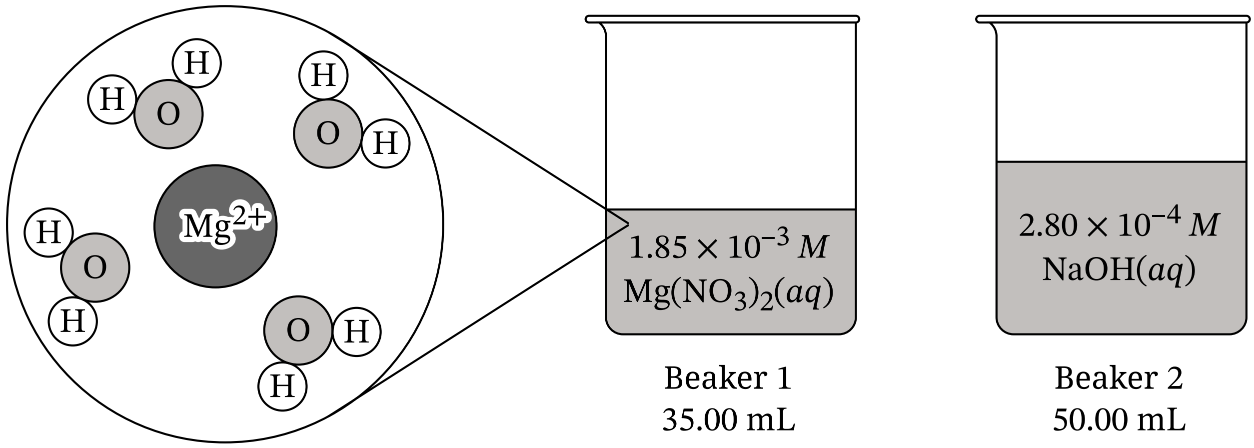


The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.

ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3}\ M$ solution of $Mg(NO_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4}\ M$ solution of $NaOH(aq)$ in beaker 2, as shown.



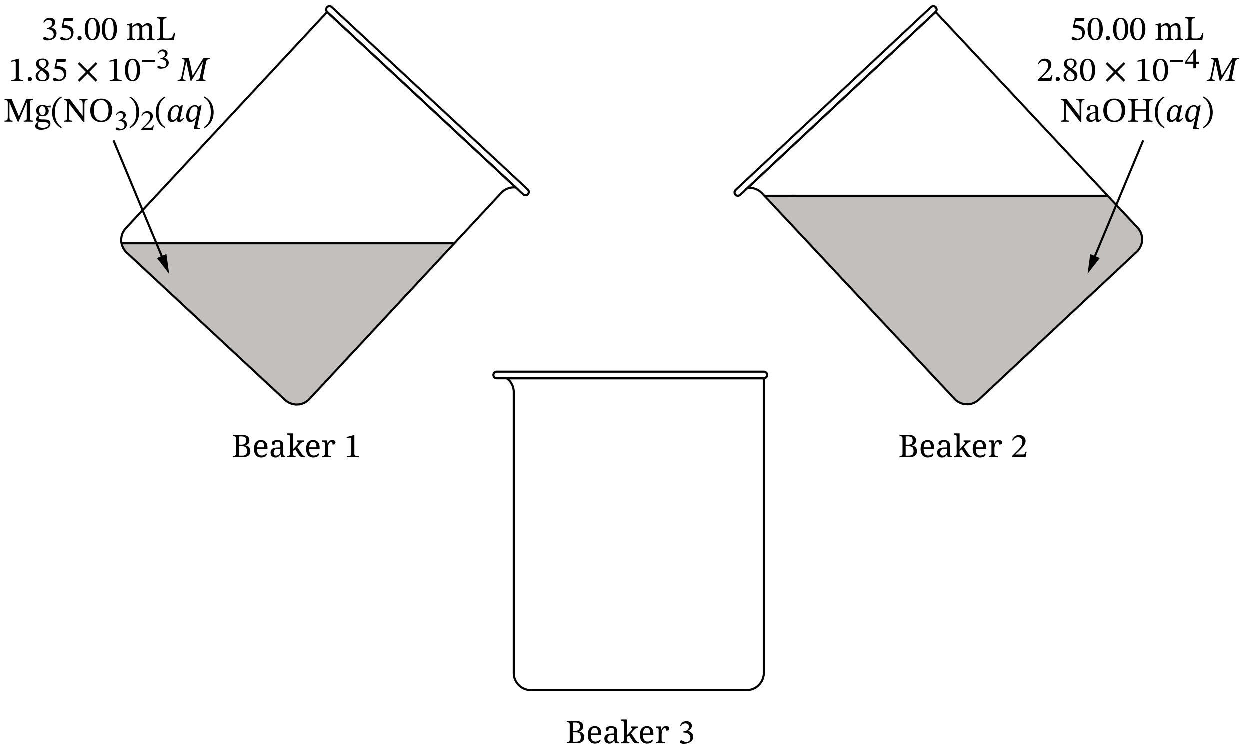
B. The particle diagram shown represents a magnesium ion, Mg^{2+}, in beaker 1. A sodium ion, Na^{+}, in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

i. The relative charge of the ions

ii. The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

D. A student combines 35.00 mL of 1.85×10^{-3} M $Mg(NO_3)_2(aq)$ with 50.00 mL of 2.80×10^{-4} M $NaOH(aq)$, as shown in the diagram. Calculate $[Mg^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



E. The dissolution of magnesium hydroxide is represented by the following equation.

$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq) \qquad K_{sp} = 5.61\times10^{-12}$$

i. Write the expression for the solubility product constant, K_{sp}.

ii. After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[OH^-] = 1.65\times10^{-4}$ M. Using your answer to part D, calculate the value of the reaction quotient, Q.

iii. Using the reaction quotient, Q, predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.

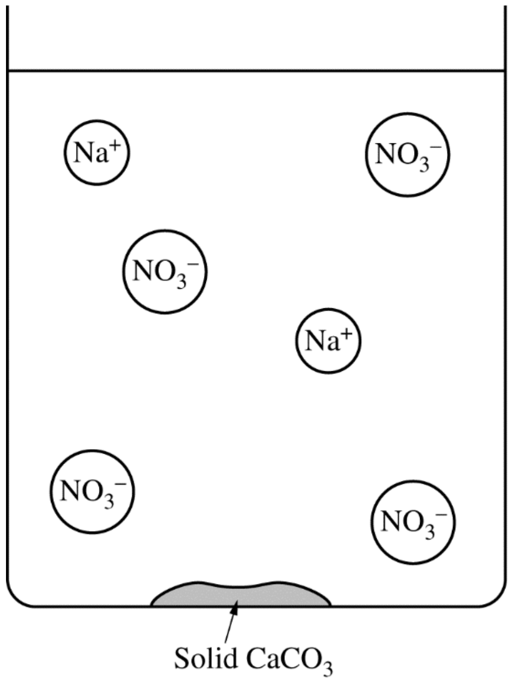
F. In a separate experiment, the student adds $HNO_3(aq)$ to decrease the pH of a saturated solution containing undissolved $Mg(OH)_2(s)$. Does the amount of undissolved $Mg(OH)_2(s)$ increase, decrease, or remain the same as the $HNO_3(aq)$ is added? Justify your answer.

3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

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

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

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

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

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

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

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

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

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

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

AP CHEMISTRY • EXERCISE SHEET

8.3 Weak Acid and Base Equilibria

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS acid 酸 • weak acid 弱酸 • ph pH 值 • base 碱 • strong acid 强酸

Objective

Build the skills to answer exam questions on **weak acid and base equilibria** (K_a and K_b).

You must be able to:

- write the K_a (or K_b) expression
- use an ICE table with the small-x approximation
- find the pH of a weak acid

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The acid-dissociation constant

For $HA \rightleftharpoons H^+ + A^-$:

$$K_a = \frac{[H^+][A^-]}{[HA]}.$$

A **small** K_a means a weak acid (little ionization).

■ The ICE + approximation

Start $[HA] = C$, $[H^+] = [A^-] = 0$; change $-x, +x, +x$. With x small, $C - x \approx C$, so

$$K_a \approx \frac{x^2}{C} \;\Rightarrow\; x = \sqrt{K_a C} = [H^+].$$

■ A worked pH

0.10 M acid, $K_a = 1.8 \times 10^{-5}$: $x = \sqrt{(1.8 \times 10^{-5})(0.10)} = \sqrt{1.8 \times 10^{-6}} = 1.34 \times 10^{-3}$, so $\text{pH} = -\log(1.34 \times 10^{-3}) = 2.87$.

■ **Bases use Kb**

For a weak base, $K_b = \dfrac{[BH^+][OH^-]}{[B]}$, and the same method gives $[OH^-]$, then pOH and pH.

2 Practice

Now apply the methods above.

2.1 Write the K_a expression for $HF \rightleftharpoons H^+ + F^-$. [1]

2.2 Does a small K_a mean a strong or weak acid? [1]

2.3 For 0.10 M acid with $K_a = 4 \times 10^{-7}$, use $x = \sqrt{K_a C}$ to find $[H^+]$. [2]

3 Exam-style questions

3.1 For a weak acid, $[H^+] \approx$ [1]

- **A** K_a
- **B** $\sqrt{K_a C}$
- **C** C
- **D** $K_a C$

3.2 A 0.20 M solution of a weak acid has $K_a = 1.0 \times 10^{-5}$.

(a) Find $[H^+]$ using the approximation. [2]

(b) Find the pH. [2]

3.3 Explain why the small-x approximation is valid for a weak acid but not for a strong acid. [2]

Solutions

2.1 $K_a = \dfrac{[\mathrm{H^+}][\mathrm{F^-}]}{[\mathrm{HF}]}$.

2.2 Weak.

2.3 $x = \sqrt{(4 \times 10^{-7})(0.10)} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$ M.

3.1 **B** — $[\mathrm{H^+}] \approx \sqrt{K_a C}$.

3.2 (a) $[\mathrm{H^+}] = \sqrt{(1.0 \times 10^{-5})(0.20)} = \sqrt{2.0 \times 10^{-6}} = 1.41 \times 10^{-3}$ M. (b) $\mathrm{pH} = -\log(1.41 \times 10^{-3}) = 2.85$.

3.3 A weak acid ionizes only slightly, so x is tiny compared to C and $C - x \approx C$; a strong acid ionizes fully, so $x \approx C$ and the approximation fails.

Question 3: Version J

The following information applies to all parts.

---

3. Nitrous acid, HNO_2, is a weak acid that ionizes according to Equation 1.

$$\text{Equation 1: } HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq) \quad K_a = 5.6\times10^{-4} \text{ at } 298 \text{ K}$$

Part A

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $HNO_2(aq)$ with an initial concentration of $0.125\ M$ has a pH of 2.09.

i. **Calculate** the value of $[H_3O^+]$ in the solution. Show the work that leads to your answer.

ii. **Calculate** $[HNO_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of $0.125\ M$ $HNO_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[HNO_2] = 0.114\ M$, $[NO_2^-] = 0.0109\ M$, and $[H_3O^+] = 0.0109\ M$.

i. **Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.

ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

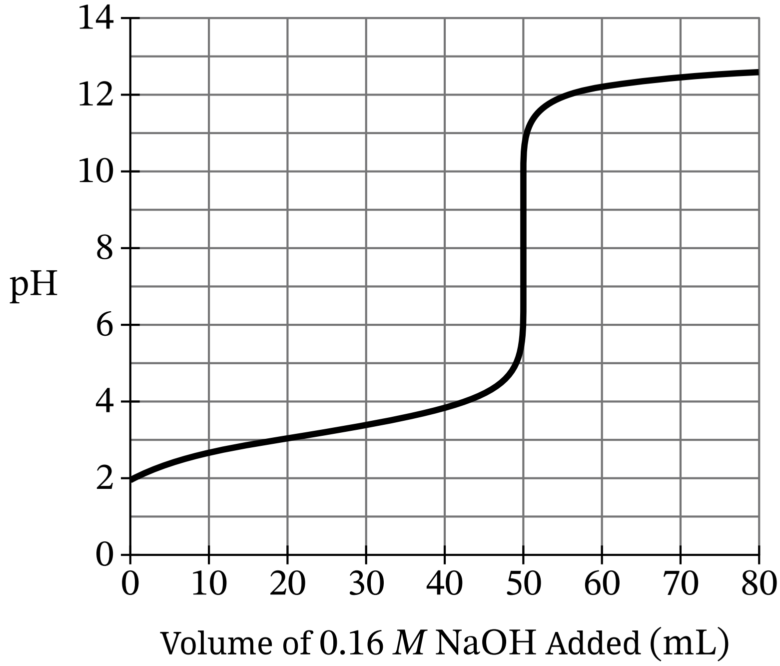
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $HNO_2(aq)$ in the bottle, the student titrates 35.0 mL of the $HNO_2(aq)$ with 0.16 M $NaOH(aq)$ at 298 K, which reacts according to Equation 2.

Equation 2: $HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$

The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $HNO_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[HNO_2] > [NO_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a; the autoionization of water, K_w; and the neutralization reaction represented by Equation 2, K_2.

Table 1

Chemical Equation	Equilibrium Constant
$HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$	$K_2 =\ ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

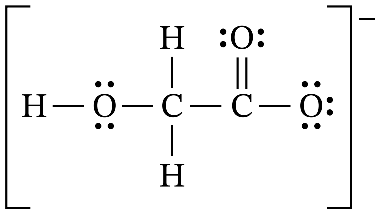
Table 2

Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $HNO_2(aq)$ solution and titrating the solution with 0.16 M $NaOH(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

7. Answer the following questions about the glycolate ion, $C_2H_3O_3^-$, which acts as a base in aqueous solution. A Lewis diagram for the ion is provided.



A. On the Lewis diagram in part A, circle the atom that accepts the proton when the glycolate ion reacts with water.

When the glycolate ion reacts with water, it forms glycolic acid, $HC_2H_3O_3$, according to the following equation. The K_b expression for the reaction is provided.

$$C_2H_3O_3^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_3(aq) + OH^-(aq) \qquad K_b = \frac{[HC_2H_3O_3][OH^-]}{[C_2H_3O_3^-]}$$

B. At 25°C, a 2.5 M solution of glycolate is found to have $[OH^-] = 1.3 \times 10^{-5}\ M$.

i. Calculate the value of K_b for the glycolate ion.

ii. Using your answer to part B (i), calculate the value of K_a for glycolic acid at 25°C.

Glycolic acid can be produced from the hydrolysis of methyl glycolate, $C_3H_6O_3$. A proposed mechanism for the reaction is given.

Step 1: $C_3H_6O_3 + H_3O^+ \rightleftharpoons C_2H_5O_3^+ + CH_3OH$

Step 2: $\underline{C_2H_5O_3^+ + H_2O \rightleftharpoons HC_2H_3O_3 + H_3O^+}$

Overall: $C_3H_6O_3 + H_2O \rightleftharpoons HC_2H_3O_3 + CH_3OH$

C. A student claims that H_3O^+ is a catalyst for the reaction. Do you agree or disagree? Justify your answer based on the mechanism given.

STOP

END OF EXAM

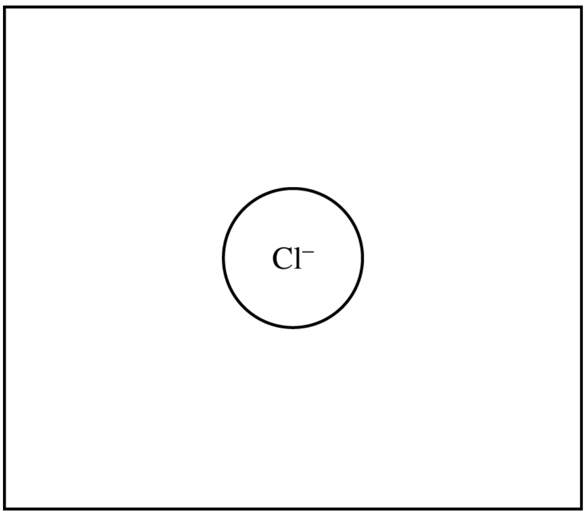
. HCl is a molecular gas as a pure substance but acts as an acid in aqueous solution.

(a) A sample of $HCl(g)$ is stored in a rigid 6.00 L container at 7.45 atm and 296 K.

(i) Calculate the number of moles of $HCl(g)$ in the container.

(ii) The rigid 6.00 L container of $HCl(g)$ is cooled to a temperature of 271 K. Calculate the new pressure, in atm, of the $HCl(g)$.

(b) When HCl ionizes in aqueous solution, $Cl^{-}(aq)$ ions are formed. In the following box, draw <u>three</u> water molecules with proper orientation around the Cl^{-} ion. Use  to represent water molecules.



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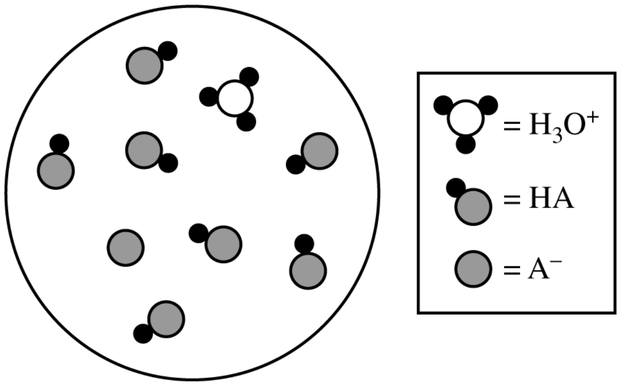
Continue your response to **QUESTION 5** on this page.

Acid (HA)	Anion (A^-)	K_a Value
HNO_2	NO_2^-	5.6×10^{-4}
HCl	Cl^-	2.0×10^7
$HClO_4$	ClO_4^-	1.6×10^{15}

The K_a values for three acids are shown in the preceding table.

(c) The following particulate diagram represents the ionization of one of the acids in the data table. Water molecules have been omitted for clarity. Which acid (HNO_2, HCl, or $HClO_4$) is represented in the diagram? Justify your answer using the information in the table.



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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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

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

$$HCOOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCOO^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

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

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

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

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 4** on this page.

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

O

H C O H

$$H_2NNH_2(aq) + H_2O(l) \rightleftarrows H_2NNH_3^+(aq) + OH^-(aq) \qquad K_b = 1.3 \times 10^{-6}$$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 M $HCOOH(aq)$.

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

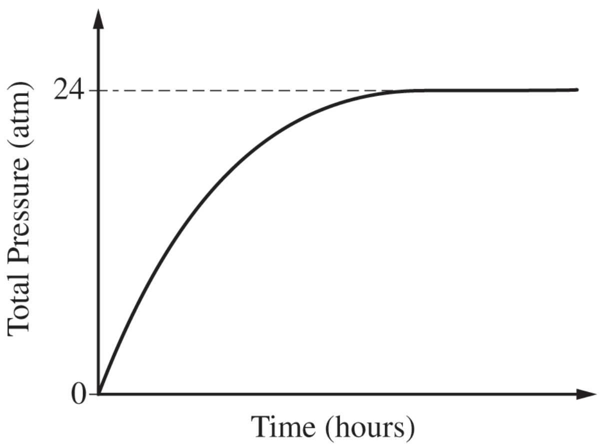
(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

GO ON TO THE NEXT PAGE.

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

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$

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



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

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

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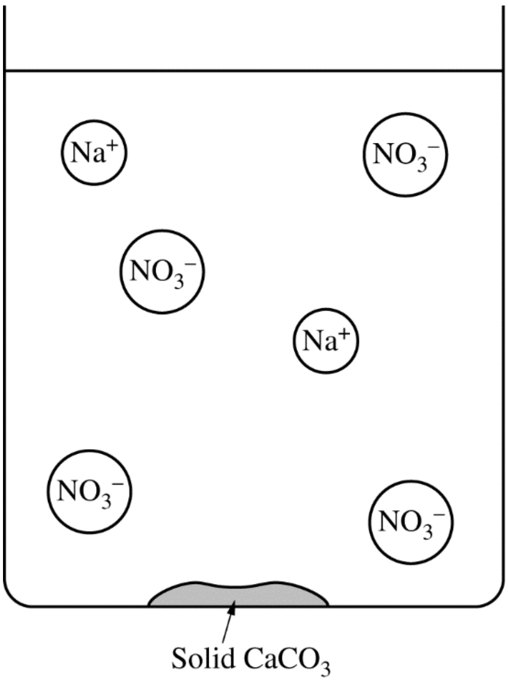
3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

$$HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$$

5. The ionization of $HF(aq)$ in water is represented by the equation above. In a 0.0350 M $HF(aq)$ solution, the percent ionization of HF is 13.0 percent.

   (a) Two particulate representations of the ionization of HF molecules in the 0.0350 M $HF(aq)$ solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)

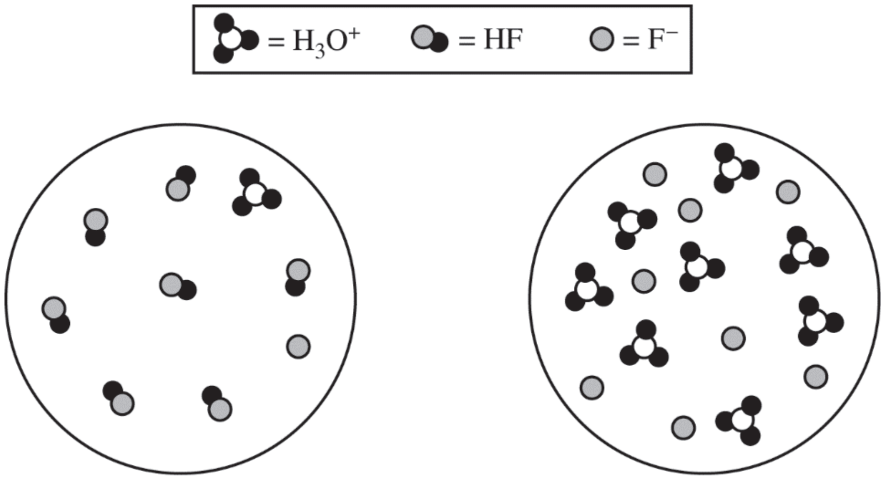


Figure 1 Figure 2

   (b) Use the percent ionization data above to calculate the value of K_a for HF.

   (c) If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M $HF(aq)$, will the percent ionization of $HF(aq)$ in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

AP Chemistry: **2016**

$$C_6H_5OH(aq) + H_2O(l) \rightleftarrows C_6H_5O^-(aq) + H_3O^+(aq) \qquad K_a = 1.12 \times 10^{-10}$$

4. Phenol is a weak acid that partially dissociates in water according to the equation above.

   (a) What is the pH of a 0.75 M $C_6H_5OH(aq)$ solution?

   (b) For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle <u>each</u> pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

1 2 3 4 5 6 7 8 9 10 11 12 13 14

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

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

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

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

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

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

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

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

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

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

AP CHEMISTRY • EXERCISE SHEET

8.4 Acid-Base Reactions and Buffers

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS buffer 缓冲溶液 • ph pH 值 • acid 酸 • weak acid 弱酸 • base 碱

Objective

Build the skills to answer exam questions on **acid-base reactions and buffers** — the idea of a buffer.

You must be able to:

- describe a **buffer 缓冲溶液** (a weak acid + its conjugate base)
- explain how a buffer resists pH change
- identify a buffer mixture

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

What a buffer is

A **buffer** is a mixture of a **weak acid and its conjugate base** (or a weak base and its conjugate acid) in comparable amounts. It **resists** changes in pH when small amounts of acid or base are added.

How it resists acid

The conjugate **base** part neutralizes added H^+: $A^- + H^+ \rightarrow HA$. So added acid is mopped up and pH barely moves.

How it resists base

The weak **acid** part neutralizes added OH^-: $HA + OH^- \rightarrow A^- + H_2O$.

Identifying a buffer

A buffer needs **both** members of a conjugate pair. $CH_3COOH + CH_3COONa$ is a buffer; $HCl + NaCl$ is **not** (HCl is strong, no weak-acid reservoir).

2 Practice

Now apply the methods above.

2.1 What two components make a buffer? [1]

2.2 Which part of a buffer neutralizes added H^+? [1]

2.3 Is $HCl + NaCl$ a buffer? Give a reason. [2]

3 Exam-style questions

3.1 A buffer is made from a weak acid and its [1]

- **A** conjugate base
- **B** strong acid
- **C** metal
- **D** water only

3.2 A buffer contains CH_3COOH and CH_3COO^-.

(a) Write the reaction when a small amount of OH^- is added. [2]

(b) Explain why the pH changes only slightly. [2]

3.3 State which of these is a buffer and why: (i) $NH_3 + NH_4Cl$; (ii) $NaOH + NaCl$. [2]

Solutions

2.1 A weak acid and its conjugate base (in comparable amounts).

2.2 The conjugate base.

2.3 No — HCl is a strong acid with no weak-acid reservoir and Cl^- is not a base, so it cannot resist pH change both ways.

3.1 **A** — its conjugate base.

3.2 (a) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. (b) The weak acid neutralizes the added base, so free OH^- is consumed and the pH stays nearly constant.

3.3 (i) is a buffer — NH_3 (weak base) with its conjugate acid NH_4^+; (ii) is not — NaOH is a strong base with no conjugate weak-acid partner.

2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O.

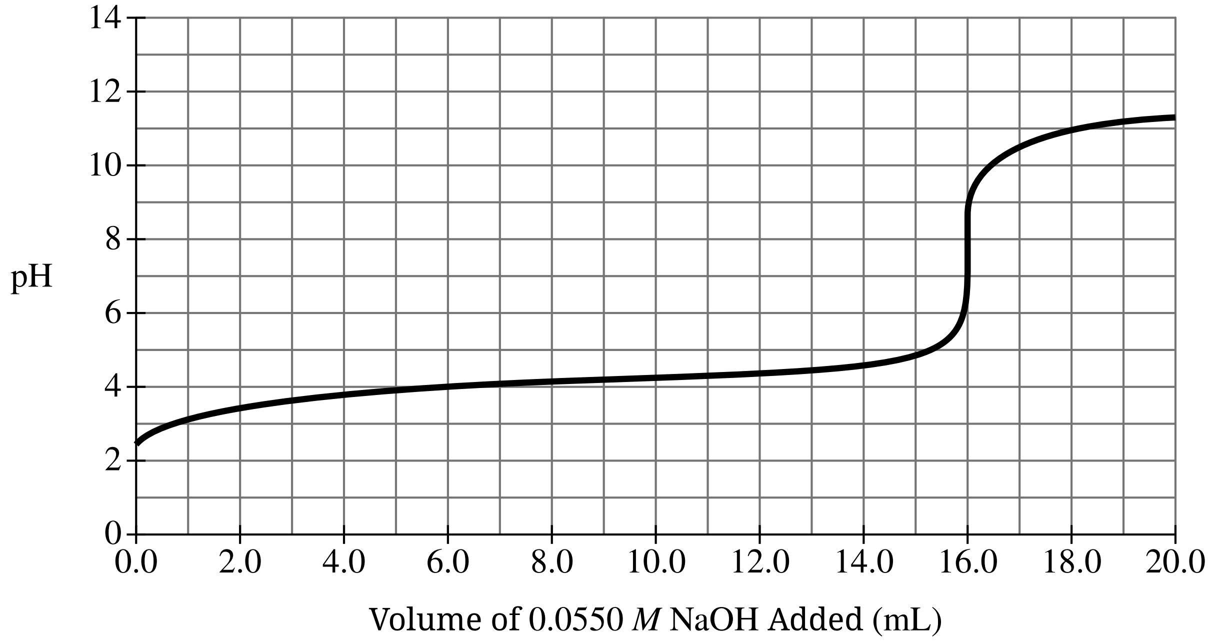
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $\mathrm{HAsc}(aq)$, acts as a weak acid, as shown in the equation.

$$\mathrm{HAsc}(aq) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{Asc^-}(aq)$$

The following titration curve was produced when a 10.0 mL sample of $\mathrm{HAsc}(aq)$ was titrated using 0.0550 M $\mathrm{NaOH}(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate $\mathrm{p}K_a$ of ascorbic acid.

iii. What is the value of the ratio $\dfrac{[\mathrm{Asc^-}]}{[\mathrm{HAsc}]}$ when the pH of the solution is 4.7?

C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^-, as represented by the following equation.

$$\text{HAsc} + I_3^- \rightarrow \text{DHAsc} + 3\ I^- + 2\ H^+$$

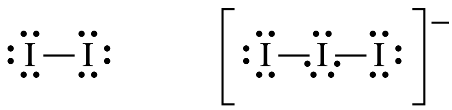
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^-, producing the following data.

Trial	[HAsc] (M)	$[I_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

i. The rate law for the reaction is $rate = k[\text{HAsc}][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.

ii. Calculate the value of the rate constant, k, for the reaction. Include units with your answer.

D. The triiodide ion, I_3^-, is significantly more soluble in water than elemental iodine, I_2, is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



I_2 $\qquad$ I_3^-

. A student is asked to prepare a buffer solution made with equimolar amounts of $CH_3NH_2(aq)$ and $CH_3NH_3Cl(s)$. The student uses 25.00 mL of 0.100 M $CH_3NH_2(aq)$, which contains 0.00250 mol of CH_3NH_2, to make the buffer.

(a) Calculate the mass of $CH_3NH_3Cl(s)$ that contains 0.00250 mol of CH_3NH_3Cl.

The student has the following materials and equipment available.

- Distilled water
- 0.100 M $CH_3NH_2(aq)$
- Solid CH_3NH_3Cl
- Electronic balance
- Weighing paper
- 50.00 mL buret
- 50 mL beaker
- 10.0 mL graduated cylinder
- Small spatula
- Pipets
- pH meter

(b) The following table contains a partial procedure for making the buffer solution. Fill in steps 1 and 4 to complete the procedure using only materials and equipment selected from the choices given. (Not all materials listed will be used. Assume that all appropriate safety measures are already in place.)

Step	Procedure
1	
2	Place the solid in the 50 mL beaker.
3	Clean the buret and rinse with distilled water.
4	
5	Use the buret to add 25.00 mL of 0.100 M $CH_3NH_2(aq)$ to the beaker.
6	Mix well.
7	Check the pH with the pH meter.

GO ON TO THE NEXT PAGE.

The value of K_b for $CH_3NH_2(aq)$ is 4.4×10^{-4}, and the pH of the buffer the student prepared is 10.64.

(c) The student prepares a second buffer solution. The student uses 25.00 mL of 0.050 *M* $CH_3NH_2(aq)$ instead of 25.00 mL of 0.100 *M* $CH_3NH_2(aq)$, and half the mass of $CH_3NH_3Cl(s)$ that was used in the first buffer. Is the pH of the second buffer greater than, less than, or equal to the pH of the first buffer? Justify your answer.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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

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

. A student reacts 0.300 g of methyl salicylate ($C_8H_8O_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($HC_7H_5O_3$).

(a) For every 1 mole of $C_8H_8O_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($HC_7H_5O_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $HC_7H_5O_3$ that could be produced in this reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

As part of the experimental procedure to purify the $HC_7H_5O_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $HC_7H_5O_3$ are given in the following table.

Properties of Salicylic Acid ($HC_7H_5O_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $HC_7H_5O_3$. The student suggests that some of the $HC_7H_5O_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $HC_7H_5O_3$ (molar mass 138.12 g / mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

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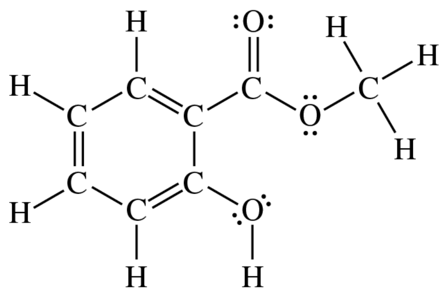
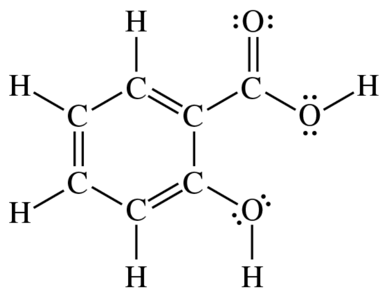
Continue your response to **QUESTION 1** on this page.

The structures and melting points for methyl salicylate and salicylic acid are shown.



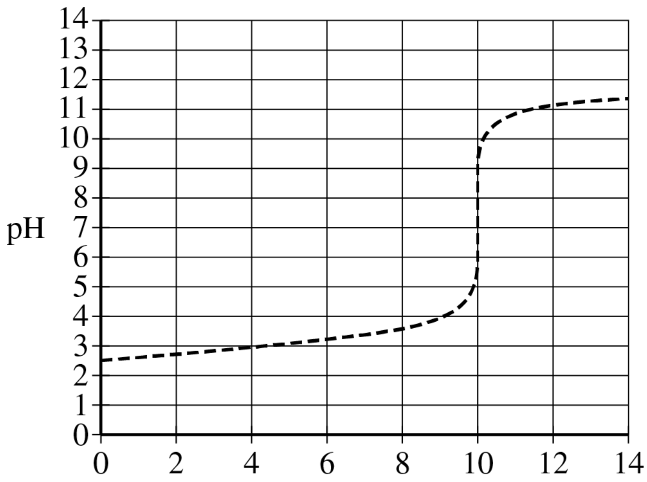
Methyl Salicylate
Melting Point: –9°C



Salicylic Acid
Melting Point: 159°C

(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $HC_7H_5O_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



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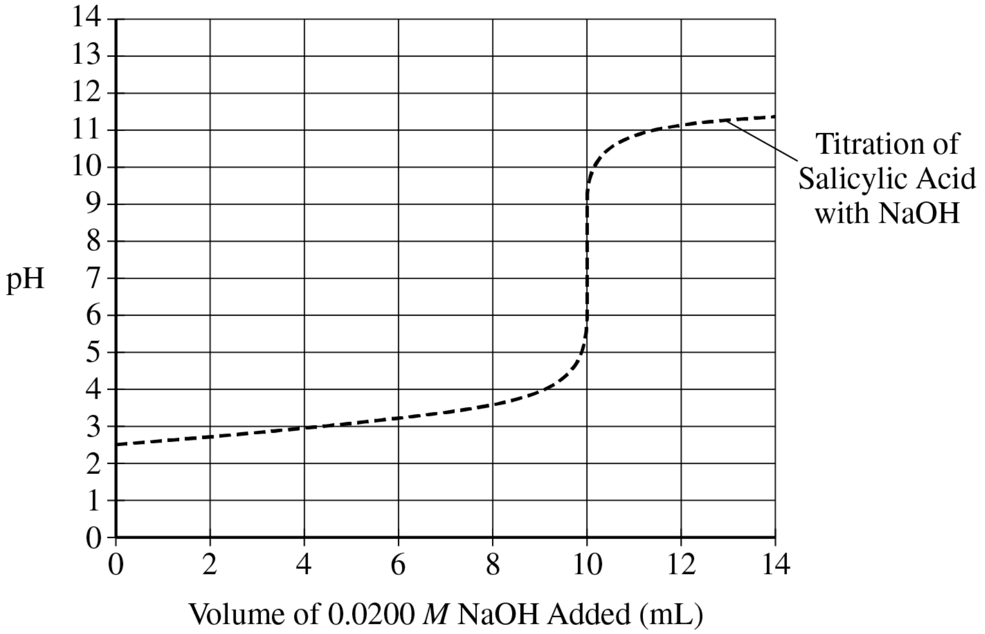
Continue your response to **QUESTION 1** on this page.

(e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. ______________

(f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.

(g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5}. Calculate the value of pK_a for benzoic acid.

(h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 M benzoic acid solution with 0.0200 M NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 M salicylic acid. The initial pH of the benzoic acid solution is 3.11.



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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

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

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$$HCOOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCOO^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

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

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

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

GO ON TO THE NEXT PAGE.

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

	O		
H	C	O	H

$$H_2NNH_2(aq) + H_2O(l) \rightleftarrows H_2NNH_3^{+}(aq) + OH^{-}(aq) \qquad K_b = 1.3 \times 10^{-6}$$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

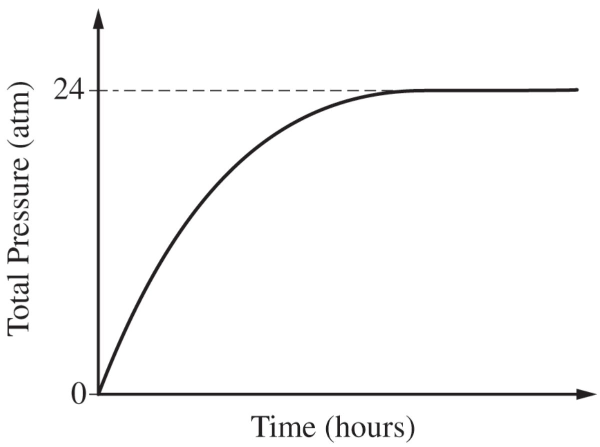
(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

GO ON TO THE NEXT PAGE.

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

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$

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



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

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

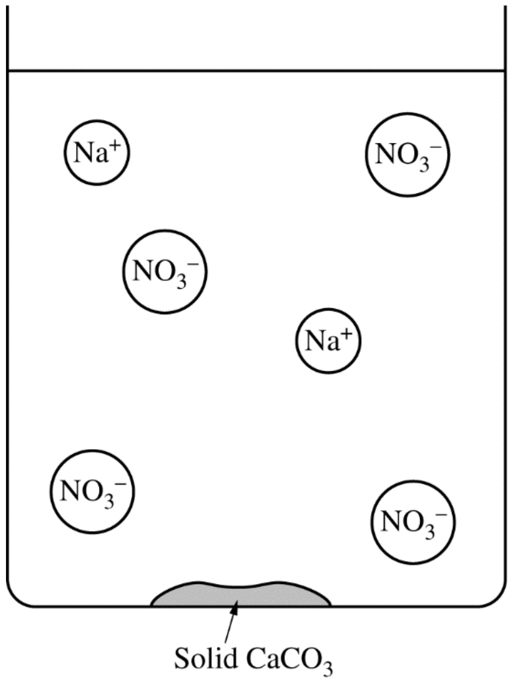
GO ON TO THE NEXT PAGE.

3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 *M* $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

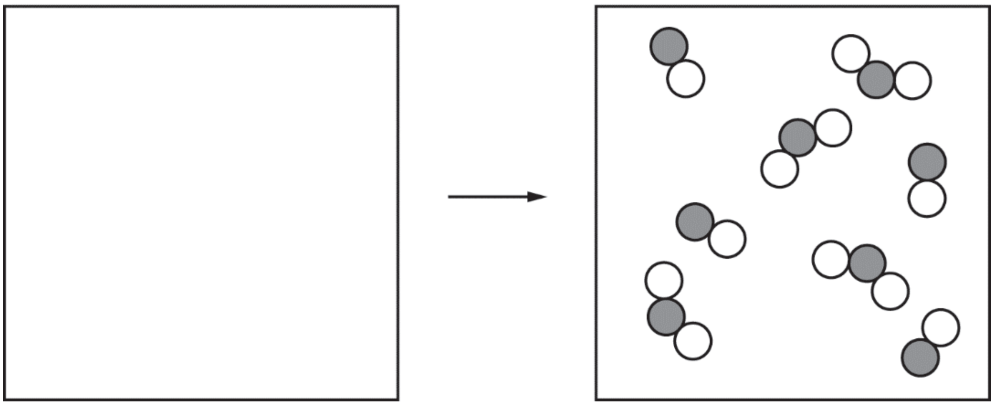
(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

   (a) The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $NO(g)$ and $O_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.

Oxygen atom = ○	Nitrogen atom = ●



Reactant Mixture　　　　Product Mixture

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
-40.4 kJ/mol$_{rxn}$	-138.5 J/(K·mol$_{rxn}$)	0.87 kJ/mol$_{rxn}$

   (b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

      (i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

      (ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

   (c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$N_2O_3(g)$ reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

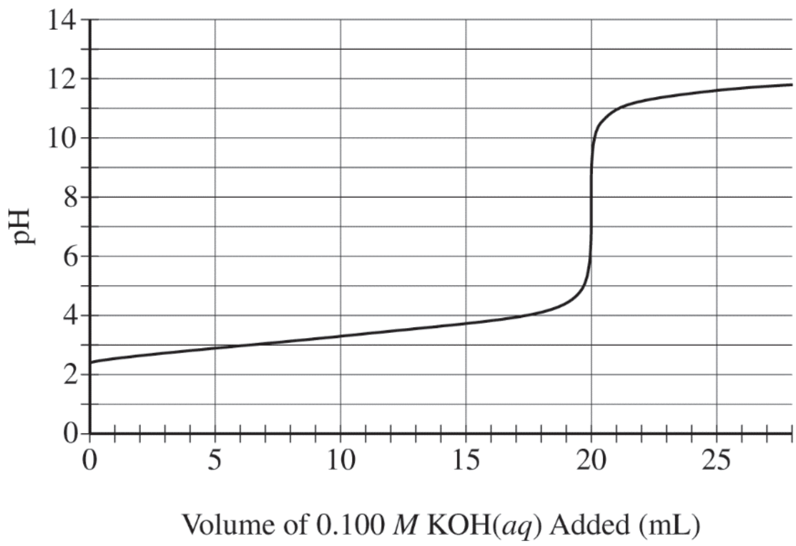
H O N O

(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

To produce an aqueous solution of HNO_2, the student bubbles $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $KOH(aq)$. The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The following titration curve shows the change in pH of the solution during the titration.



(e) Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

(ii) estimate the value of pK_a for $HNO_2(aq)$

(f) During the titration, after a volume of 15 mL of 0.100 M $KOH(aq)$ has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

$$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

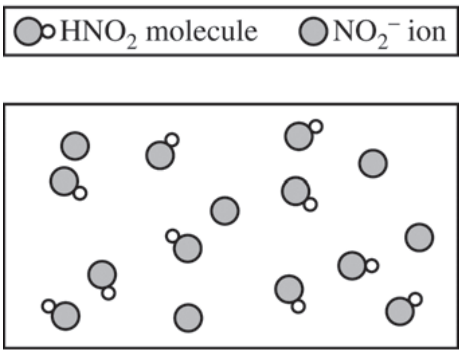
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 M $NaOH(aq)$ the student should add to 100. mL of 0.100 M $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 M $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

(b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

(c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only   Entropy only   Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.

(f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.

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

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

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

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

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

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

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

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

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

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

8.5 Acid-Base Titrations

Name: ______________ Class: __________ Date: ____________ **Total: 10 marks**

KEY WORDS titration curve 滴定曲线 • equivalence point 等当点 • acid 酸 • ph pH 值 • weak acid 弱酸

Objective

Build the skills to answer exam questions on **acid-base titrations** — reading the titration curve.

You must be able to:

- identify the **equivalence point** 等当点 on a titration curve
- locate the **half-equivalence point** where pH = pK_a
- describe the curve shape for strong and weak acids

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The equivalence point

The **equivalence point** is where the moles of added base exactly equal the moles of acid. On the curve it is the **steep vertical jump** in pH.

■ Equivalence pH depends on the acids

- **Strong acid + strong base** → equivalence pH = 7.
- **Weak acid + strong base** → equivalence pH > 7 (the conjugate base is basic).

■ The half-equivalence point

At the **half-equivalence point** (half the base added), [HA] = [A^-], so

$$\mathrm{pH} = \mathrm{p}K_a.$$

This is the flattest part (the buffer region) and a quick way to read pK_a off a curve.

■ Reading Ka from a curve

Find the half-equivalence volume (half the equivalence volume), read its pH — that is pK_a, and $K_a = 10^{-\mathrm{p}K_a}$.

2 Practice

Now apply the methods above.

2.1 What is true of the moles of acid and base at the equivalence point? [1]

2.2 At the half-equivalence point, pH equals what? [1]

2.3 For a strong acid-strong base titration, what is the equivalence pH? [1]

3 Exam-style questions

3.1 The equivalence point of a weak acid titrated with a strong base has a pH that is [1]

- **A** exactly 7
- **B** greater than 7
- **C** less than 7
- **D** zero

3.2 A weak acid is titrated with NaOH. The equivalence point is at 20.0 mL of base.

(a) At what volume is the half-equivalence point? [1]

(b) If the pH there is 4.7, find pK_a and K_a. [3]

3.3 Explain why the equivalence pH of a weak acid-strong base titration is above 7. [2]

Solutions

2.1 They are equal (in the stoichiometric ratio).

2.2 pK_a.

2.3 7.

3.1 **B** — greater than 7.

3.2 (a) 10.0 mL (half of 20.0). (b) pK_a = pH = 4.7; $K_a = 10^{-4.7} = 2.0 \times 10^{-5}$.

3.3 At equivalence all the acid has become its conjugate base A^-, which is a weak base and reacts with water to give OH^-, raising the pH above 7.

Question 3: Version J

The following information applies to all parts.

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3. Nitrous acid, HNO_2, is a weak acid that ionizes according to Equation 1.

$$\text{Equation 1: } HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq) \quad K_a = 5.6\times10^{-4} \text{ at } 298\text{ K}$$

Part A

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $HNO_2(aq)$ with an initial concentration of $0.125\ M$ has a pH of 2.09.

i. **Calculate** the value of $[H_3O^+]$ in the solution. Show the work that leads to your answer.

ii. **Calculate** $[HNO_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of $0.125\ M$ $HNO_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[HNO_2] = 0.114\ M$, $[NO_2^-] = 0.0109\ M$, and $[H_3O^+] = 0.0109\ M$.

i. **Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.

ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

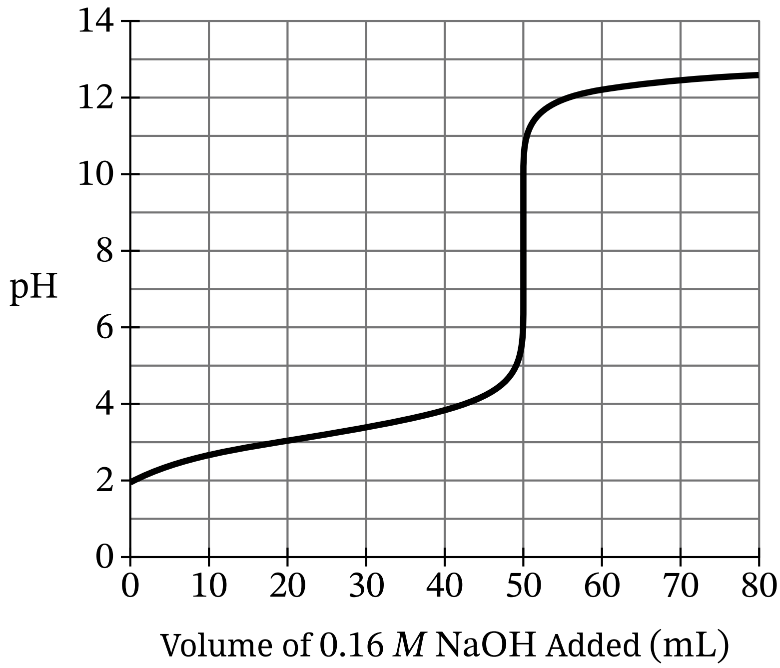
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $HNO_2(aq)$ in the bottle, the student titrates 35.0 mL of the $HNO_2(aq)$ with 0.16 M $NaOH(aq)$ at 298 K, which reacts according to Equation 2.

$$\text{Equation 2: } HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $HNO_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[HNO_2] > [NO_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a; the autoionization of water, K_w; and the neutralization reaction represented by Equation 2, K_2.

Table 1

Chemical Equation	Equilibrium Constant
$HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$	$K_2 = \ ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $HNO_2(aq)$ solution and titrating the solution with 0.16 M $NaOH(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O.

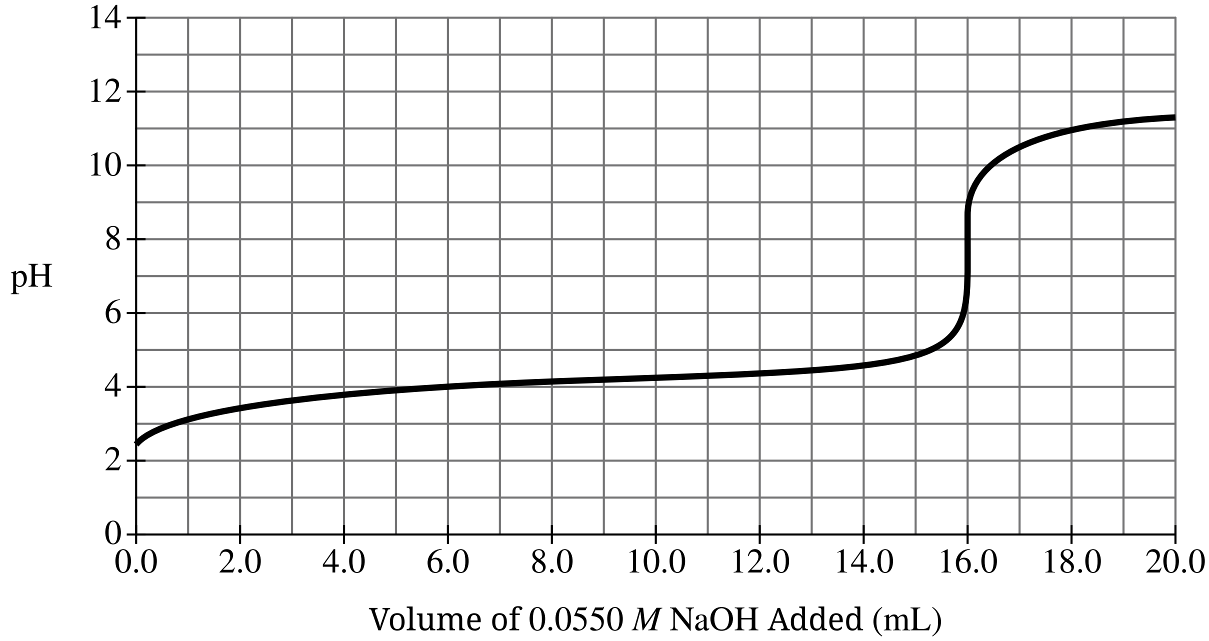
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $HAsc(aq)$, acts as a weak acid, as shown in the equation.

$$HAsc(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Asc^-(aq)$$

The following titration curve was produced when a 10.0 mL sample of $HAsc(aq)$ was titrated using 0.0550 M $NaOH(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate pK_a of ascorbic acid.

iii. What is the value of the ratio $\dfrac{[Asc^-]}{[HAsc]}$ when the pH of the solution is 4.7?

C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^-, as represented by the following equation.

$$\text{HAsc} + I_3^- \rightarrow \text{DHAsc} + 3\ I^- + 2\ H^+$$

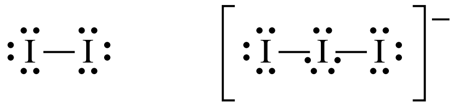
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^-, producing the following data.

Trial	[HAsc] (M)	$[I_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

i. The rate law for the reaction is $rate = k[\text{HAsc}][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to [HAsc].

ii. Calculate the value of the rate constant, k, for the reaction. Include units with your answer.

D. The triiodide ion, I_3^-, is significantly more soluble in water than elemental iodine, I_2, is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



I_2 I_3^-

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

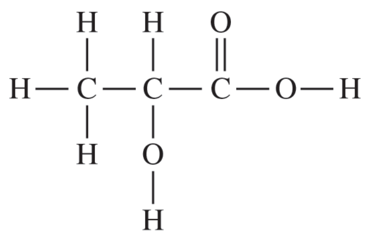
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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

$$C_3H_6O_3(aq) + NaOH(aq) \rightarrow NaC_3H_5O_3(aq) + H_2O(l)$$

1. A student is studying the reaction between lactic acid, $C_3H_6O_3$, and sodium hydroxide, NaOH, as represented in the balanced equation above.

(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.

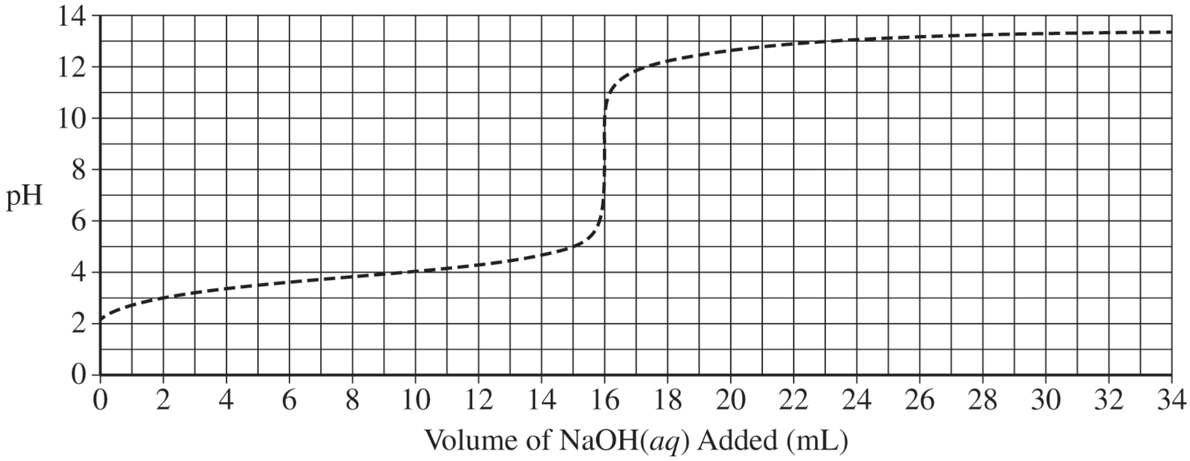


(b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g / mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

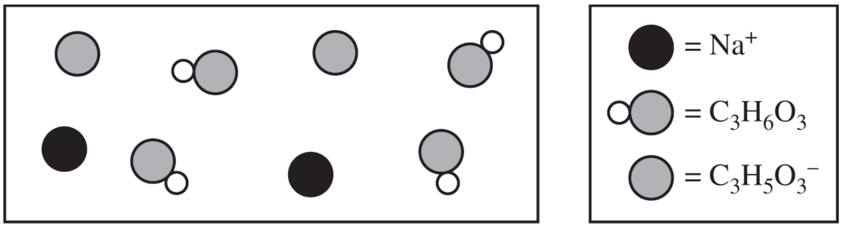
GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



(c) Use the information in the graph to determine the approximate pK_a of lactic acid. ____________



(d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

(i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.

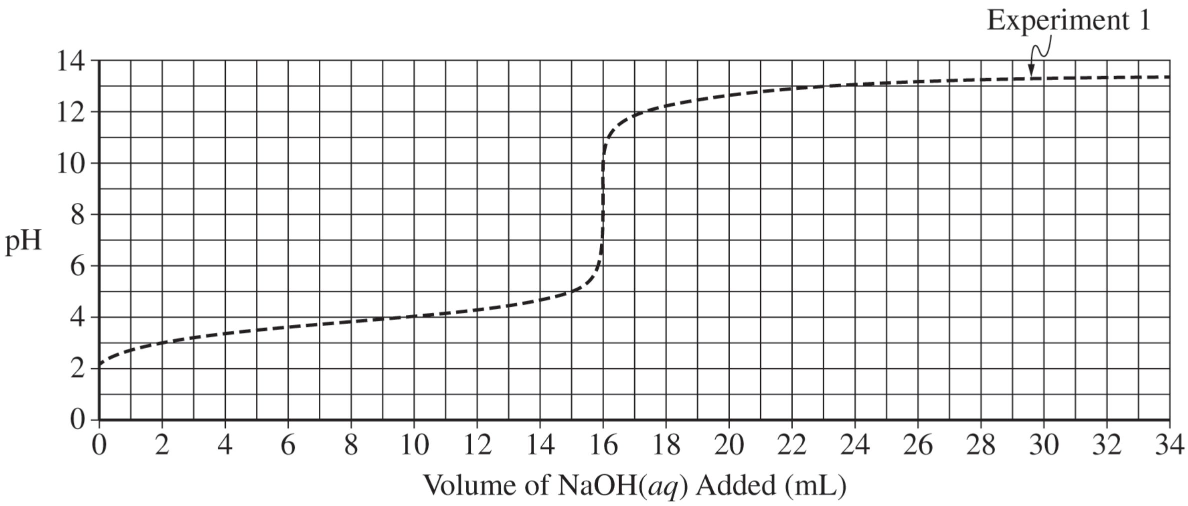
(ii) Justify your answer.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

Experiment	Mass of NaOH(s) (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

(iii) The student repeats the experiment but uses a solution of NaOH(aq) with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



(e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g / mL and that the specific heat capacity of the combined solution is 4.2 J / (g · °C).

(i) Calculate the quantity of heat produced in the reaction, in J.

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Continue your response to **QUESTION 1** on this page.

(ii) Calculate the molar enthalpy of reaction, in kJ / mol_{rxn}. Include the sign in your answer.

(iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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

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

. A student reacts 0.300 g of methyl salicylate ($C_8H_8O_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($HC_7H_5O_3$).

(a) For every 1 mole of $C_8H_8O_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($HC_7H_5O_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $HC_7H_5O_3$ that could be produced in this reaction.

GO ON TO THE NEXT PAGE.

As part of the experimental procedure to purify the $HC_7H_5O_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $HC_7H_5O_3$ are given in the following table.

Properties of Salicylic Acid ($HC_7H_5O_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $HC_7H_5O_3$. The student suggests that some of the $HC_7H_5O_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $HC_7H_5O_3$ (molar mass 138.12 g / mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

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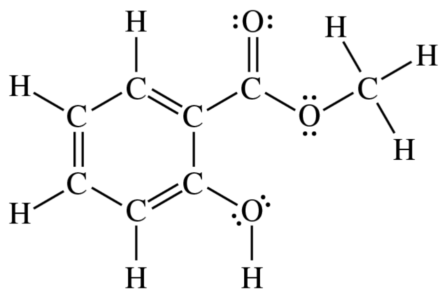
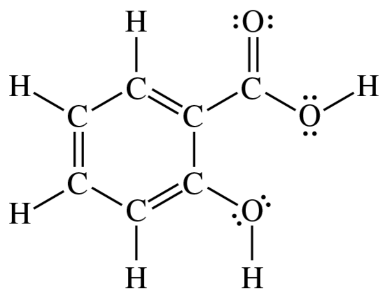
Continue your response to QUESTION 1 on this page.

The structures and melting points for methyl salicylate and salicylic acid are shown.



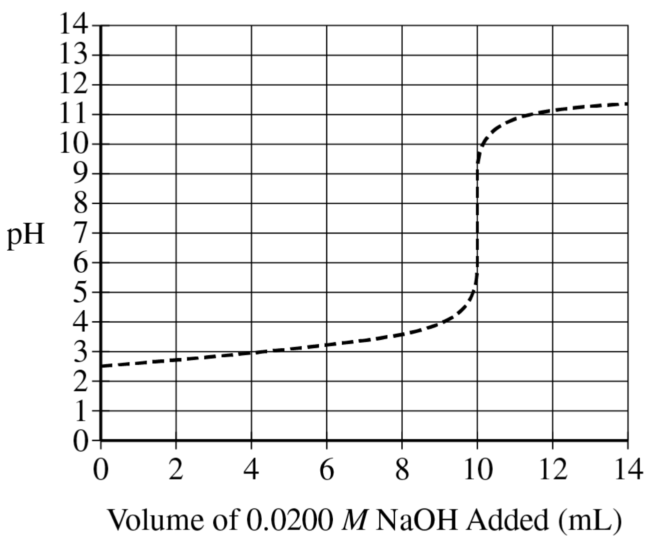
Methyl Salicylate
Melting Point: –9°C



Salicylic Acid
Melting Point: 159°C

(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $HC_7H_5O_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



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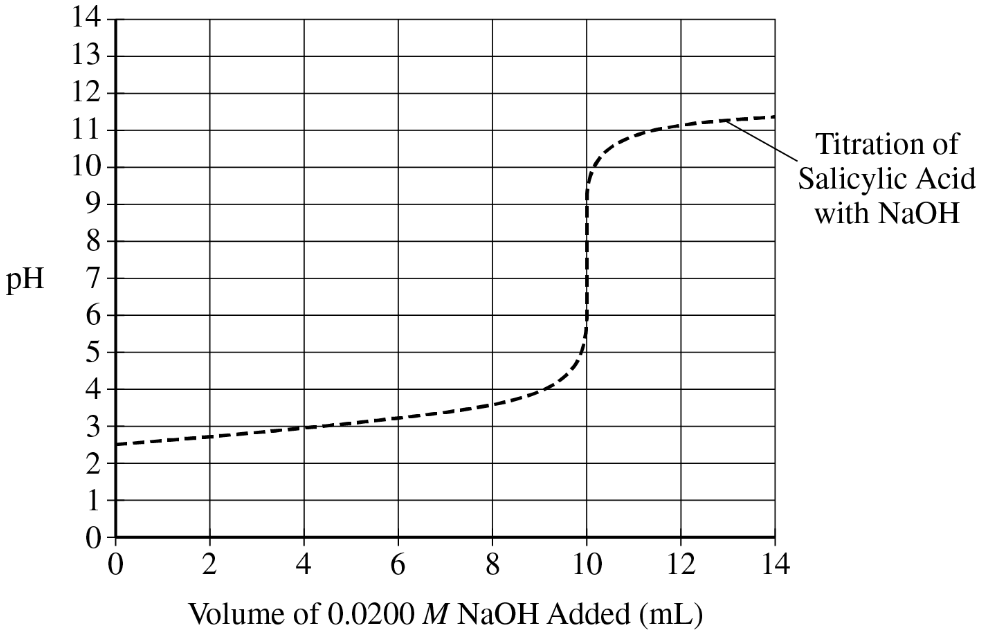
Continue your response to **QUESTION 1** on this page.

(e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. ______________

(f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.

(g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5}. Calculate the value of pK_a for benzoic acid.

(h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 M benzoic acid solution with 0.0200 M NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 M salicylic acid. The initial pH of the benzoic acid solution is 3.11.



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3. Potassium sorbate, $KC_6H_7O_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $KC_6H_7O_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 *M* HCl(*aq*) using both an indicator and a pH meter. The value of K_a for sorbic acid, $HC_6H_7O_2$, is 1.7×10^{-5}.

(a) Write the net-ionic equation for the reaction between $KC_6H_7O_2(aq)$ and $HCl(aq)$.

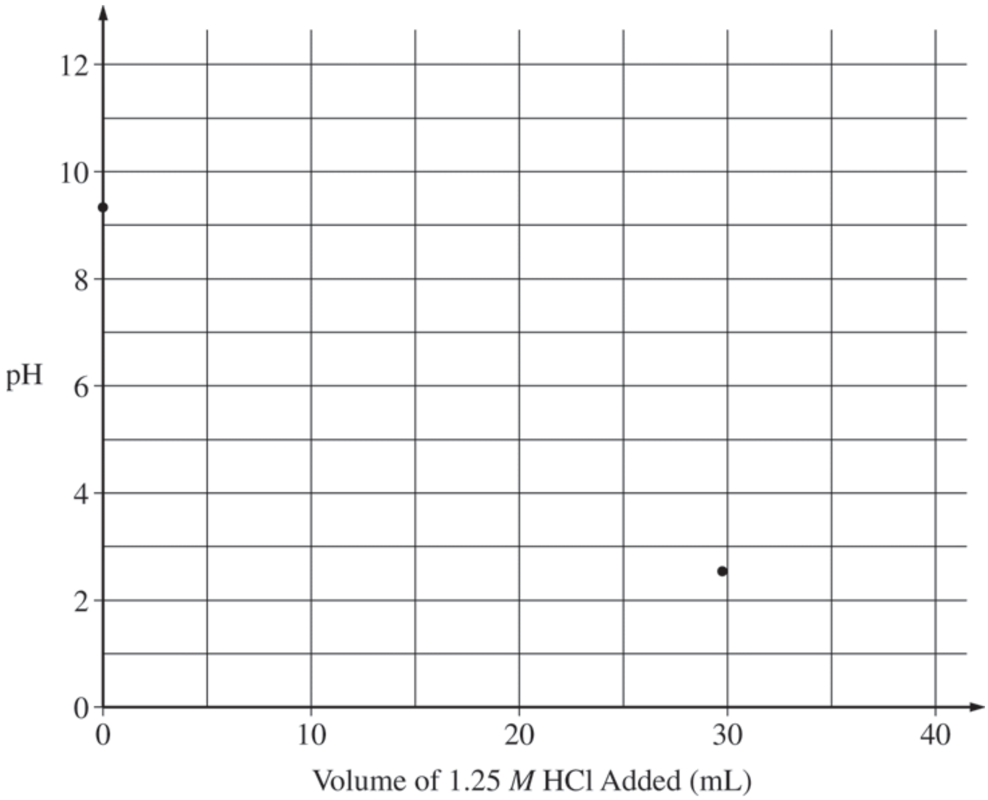
(b) A total of 29.95 mL of 1.25 *M* HCl(*aq*) is required to reach the equivalence point. Calculate $[KC_6H_7O_2]$ in the stock solution.

(c) The pH at the equivalence point of the titration is measured to be 2.54 Which of the following indicators would be the best choice for determining the end point of the titration? Justify your answer.

Indicator	pK_a
Phenolphthalein	9.3
Bromothymol blue	7.0
Methyl red	5.0
Thymol blue	2.0
Methyl violet	0.80

(d) Calculate the pH at the half-equivalence point.

(e) The initial pH and the equivalence point are plotted on the graph below. Accurately sketch the titration curve on the graph below. Mark the position of the half-equivalence point on the curve with an X.



(f) The pH of the soft drink is 3.37 after the addition of the $KC_6H_7O_2(aq)$. Which species, $HC_6H_7O_2$ or $C_6H_7O_2^-$, has a higher concentration in the soft drink? Justify your answer.

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

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

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

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

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

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

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

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

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

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

8.6 Molecular Structure of Acids and Bases

Name: ______________ Class: __________ Date: ____________ **Total: 10 marks**

KEY WORDS oxoacid 含氧酸 • acid 酸 • base 碱 • neutral 中性

Objective

Build the skills to answer exam questions on the **molecular structure of acids and bases** — what makes an acid strong.

You must be able to:

- link acid strength to bond **polarity** and bond **strength**
- compare **oxoacid 含氧酸** strength (more O atoms → stronger)
- explain trends down a group (binary acids)

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ What makes an acid ionize

An acid ionizes more easily when the bond to H is **weaker** or **more polar**, so H^+ leaves readily, and when the resulting anion is **stable**.

■ Binary acids down a group

Down a group the H–X bond gets **weaker** (larger atom), so the acid is **stronger**: $HI > HBr > HCl > HF$. Bond strength wins over polarity here.

■ Oxoacids: more oxygens = stronger

For oxoacids, more **electronegative O atoms** pull electron density away from the O–H bond, making it more polar and stabilizing the anion. So $HClO_4 > HClO_3 > HClO_2 > HClO$.

■ Central atom electronegativity

A more electronegative central atom also strengthens an oxoacid: $HClO > HBrO > HIO$.

2 Practice

Now apply the methods above.

2.1 Which is the stronger acid, HCl or HI? [1]

2.2 Which is stronger, $HClO_4$ or HClO? [1]

2.3 What two bond properties make an acid ionize more easily? [2]

3 Exam-style questions

3.1 Among oxoacids of the same central atom, more oxygen atoms make the acid [1]

- **A** weaker
- **B** stronger
- **C** neutral
- **D** basic

3.2 Rank HClO, $HClO_2$, $HClO_3$ from weakest to strongest acid, with a reason. [3]

3.3 Explain why HI is a stronger acid than HF, even though F is more electronegative. [2]

Solutions

2.1 HI.

2.2 $HClO_4$.

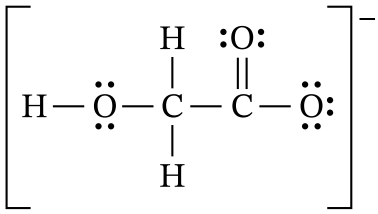
2.3 A weaker H–X bond; a more polar H–X bond.

3.1 **B** — stronger.

3.2 $HClO < HClO_2 < HClO_3$; more oxygen atoms pull electron density from the O–H bond and stabilize the anion, increasing acid strength.

3.3 The H–I bond is much weaker than H–F (I is a large atom), so H^+ is released more easily; the weaker bond outweighs F's higher electronegativity.

7. Answer the following questions about the glycolate ion, $C_2H_3O_3^-$, which acts as a base in aqueous solution. A Lewis diagram for the ion is provided.



A. On the Lewis diagram in part A, circle the atom that accepts the proton when the glycolate ion reacts with water.

When the glycolate ion reacts with water, it forms glycolic acid, $HC_2H_3O_3$, according to the following equation. The K_b expression for the reaction is provided.

$$C_2H_3O_3^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_3(aq) + OH^-(aq) \qquad K_b = \frac{[HC_2H_3O_3][OH^-]}{[C_2H_3O_3^-]}$$

B. At 25°C, a 2.5 M solution of glycolate is found to have $[OH^-] = 1.3 \times 10^{-5}\ M$.

i. Calculate the value of K_b for the glycolate ion.

ii. Using your answer to part B (i), calculate the value of K_a for glycolic acid at 25°C.

Glycolic acid can be produced from the hydrolysis of methyl glycolate, $C_3H_6O_3$. A proposed mechanism for the reaction is given.

Step 1: $C_3H_6O_3 + H_3O^+ \rightleftharpoons C_2H_5O_3^+ + CH_3OH$

Step 2: $\underline{C_2H_5O_3^+ + H_2O \rightleftharpoons HC_2H_3O_3 + H_3O^+}$

Overall: $C_3H_6O_3 + H_2O \rightleftharpoons HC_2H_3O_3 + CH_3OH$

C. A student claims that H_3O^+ is a catalyst for the reaction. Do you agree or disagree? Justify your answer based on the mechanism given.

STOP

END OF EXAM

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

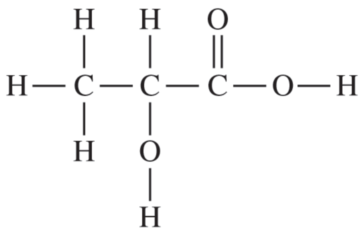
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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

$$C_3H_6O_3(aq) + NaOH(aq) \rightarrow NaC_3H_5O_3(aq) + H_2O(l)$$

1. A student is studying the reaction between lactic acid, $C_3H_6O_3$, and sodium hydroxide, NaOH, as represented in the balanced equation above.

(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.

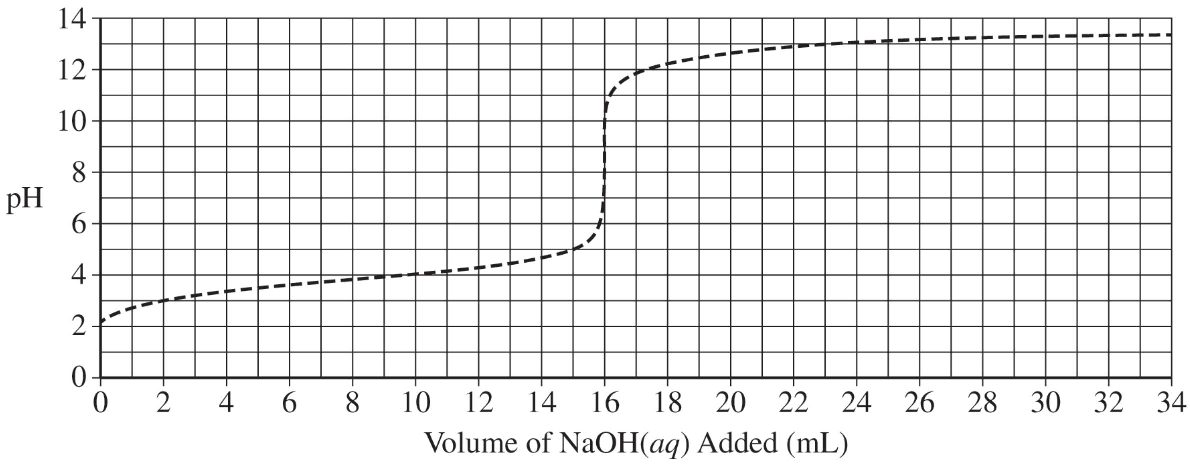


(b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g / mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

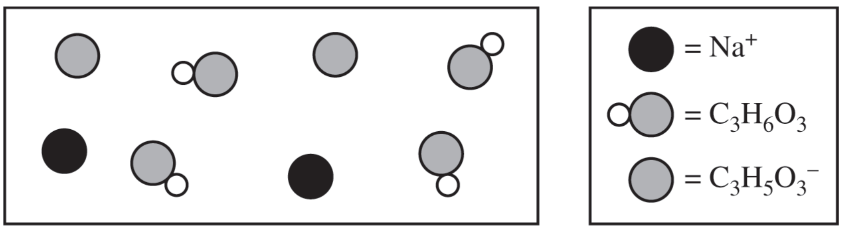
GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



(c) Use the information in the graph to determine the approximate pK_a of lactic acid. ____________



(d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

(i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.

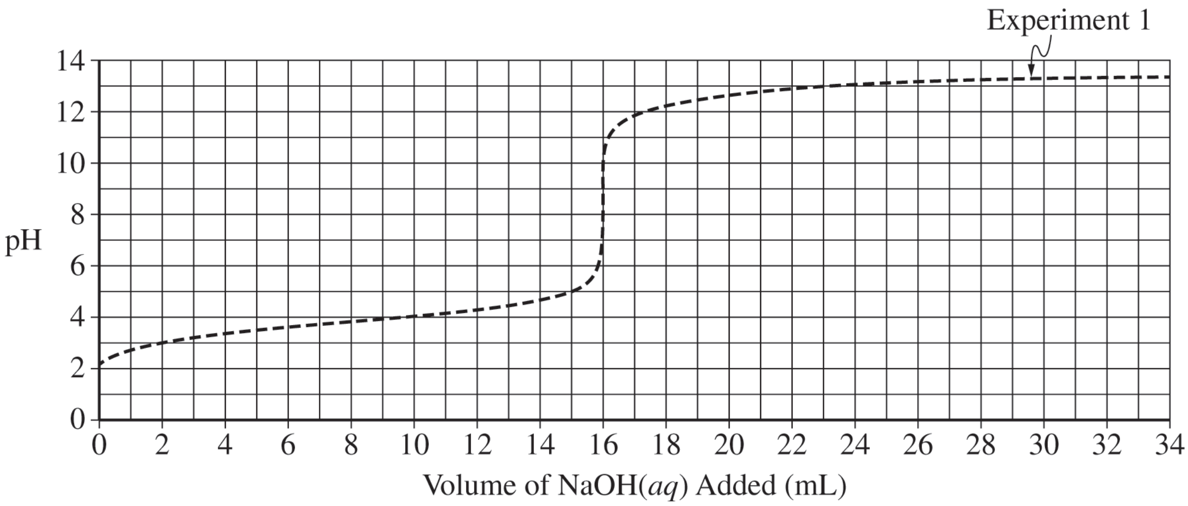
(ii) Justify your answer.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

Experiment	Mass of $NaOH(s)$ (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

(iii) The student repeats the experiment but uses a solution of $NaOH(aq)$ with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



(e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g / mL and that the specific heat capacity of the combined solution is 4.2 J / (g · °C).

(i) Calculate the quantity of heat produced in the reaction, in J.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

(ii) Calculate the molar enthalpy of reaction, in kJ / mol_{rxn}. Include the sign in your answer.

(iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

AP CHEMISTRY • EXERCISE SHEET

8.7 pH and pKa

Name: ______ Class: ______ Date: ______ **Total: 10 marks**

KEY WORDS acid 酸 • ph pH 值 • base 碱 • weak acid 弱酸 • conjugate base 共轭碱

Objective

Build the skills to answer exam questions on **pH and pKa** — comparing acid strengths.

You must be able to:

- use $pK_a = -\log K_a$
- rank acids by K_a or pK_a (smaller pK_a = stronger)
- relate pK_a to the pH where an acid is half-ionized

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ pKa

$$pK_a = -\log K_a.$$

A **larger** K_a (stronger acid) gives a **smaller** pK_a.

■ Ranking acids

A stronger acid has a bigger K_a and a **smaller** pK_a. So acid X ($pK_a = 3$) is stronger than acid Y ($pK_a = 5$).

■ pKa and half-ionization

At $pH = pK_a$, the acid is **half-ionized** ($[HA] = [A^-]$). Below that pH the acid form dominates; above it, the conjugate base dominates.

■ A worked conversion

$K_a = 1.8 \times 10^{-5}$ gives $pK_a = -\log(1.8 \times 10^{-5}) = 4.74$. Reverse: $pK_a = 3$ gives $K_a = 10^{-3}$.

2 Practice

Now apply the methods above.

2.1 Find pK_a for $K_a = 1 \times 10^{-4}$. [1]

2.2 Acid A has p$K_a = 2$, acid B has p$K_a = 6$. Which is stronger? [1]

2.3 At what pH is a weak acid half-ionized? [1]

3 Exam-style questions

3.1 A stronger acid has a [1]

- **A** larger pK_a
- **B** smaller pK_a
- **C** pK_a of exactly 7
- **D** negative K_a

3.2 Three acids have K_a values 1×10^{-3}, 1×10^{-5}, and 1×10^{-9}.

(a) Find each pK_a. [2]

(b) Rank the acids from strongest to weakest. [2]

3.3 An acid has p$K_a = 4.2$. Below pH 4.2, which form (acid or conjugate base) dominates? Explain. [2]

Solutions

2.1 p$K_a = 4$.

2.2 Acid A (p$K_a = 2$).

2.3 pH = pK_a.

3.1 **B** — a smaller pK_a.

3.2 (a) 3, 5, 9. (b) strongest to weakest: $K_a = 10^{-3}$, then 10^{-5}, then 10^{-9} (smallest pK_a first).

3.3 The acid form (HA) dominates — below pH = pK_a there is more H^+, which keeps the acid protonated.

2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O.

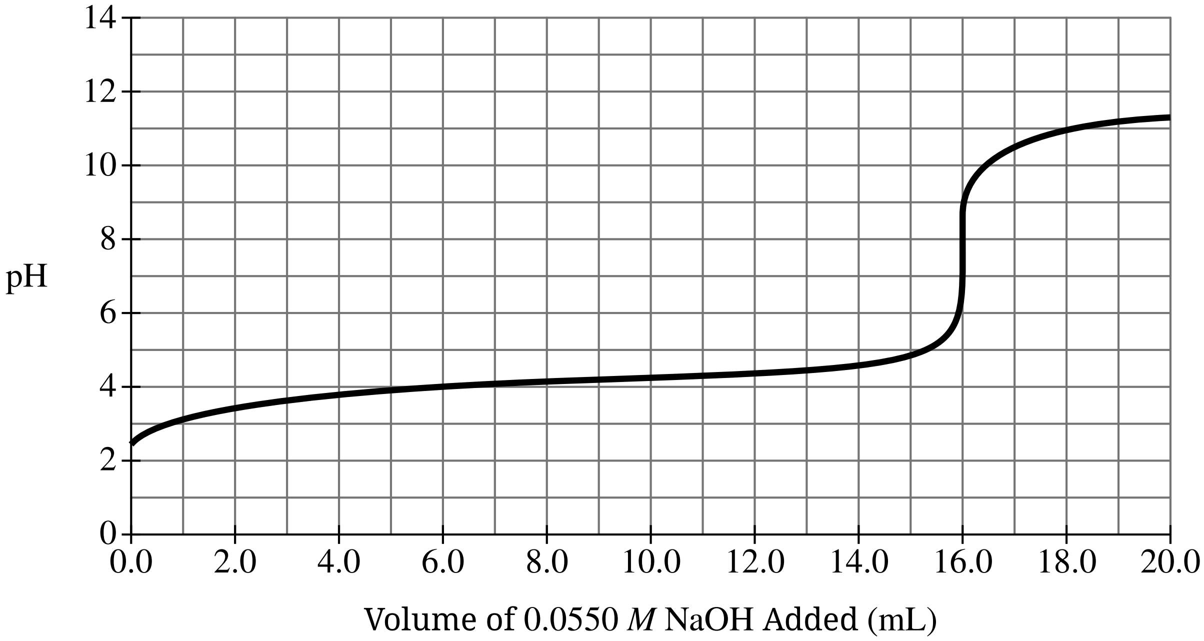
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $\text{HAsc}(aq)$, acts as a weak acid, as shown in the equation.

$$\text{HAsc}(aq) + \text{H}_2\text{O}(l) \rightleftarrows \text{H}_3\text{O}^+(aq) + \text{Asc}^-(aq)$$

The following titration curve was produced when a 10.0 mL sample of $\text{HAsc}(aq)$ was titrated using 0.0550 M $\text{NaOH}(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate $\text{p}K_a$ of ascorbic acid.

iii. What is the value of the ratio $\dfrac{[\text{Asc}^-]}{[\text{HAsc}]}$ when the pH of the solution is 4.7?

C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^-, as represented by the following equation.

$$\text{HAsc} + I_3^- \rightarrow \text{DHAsc} + 3\ I^- + 2\ H^+$$

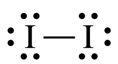
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^-, producing the following data.

Trial	[HAsc] (M)	$[I_3^-]\ (M)$	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

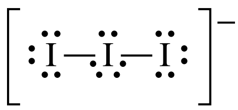
i. The rate law for the reaction is $rate = k[\text{HAsc}][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.

ii. Calculate the value of the rate constant, k, for the reaction. Include units with your answer.

D. The triiodide ion, I_3^-, is significantly more soluble in water than elemental iodine, I_2, is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



I_2



I_3^-

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

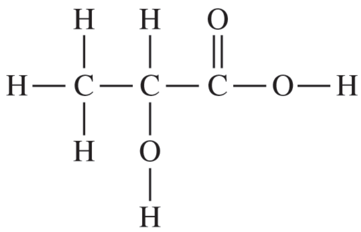
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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

$$C_3H_6O_3(aq) + NaOH(aq) \rightarrow NaC_3H_5O_3(aq) + H_2O(l)$$

1. A student is studying the reaction between lactic acid, $C_3H_6O_3$, and sodium hydroxide, NaOH, as represented in the balanced equation above.

(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.



(b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g / mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

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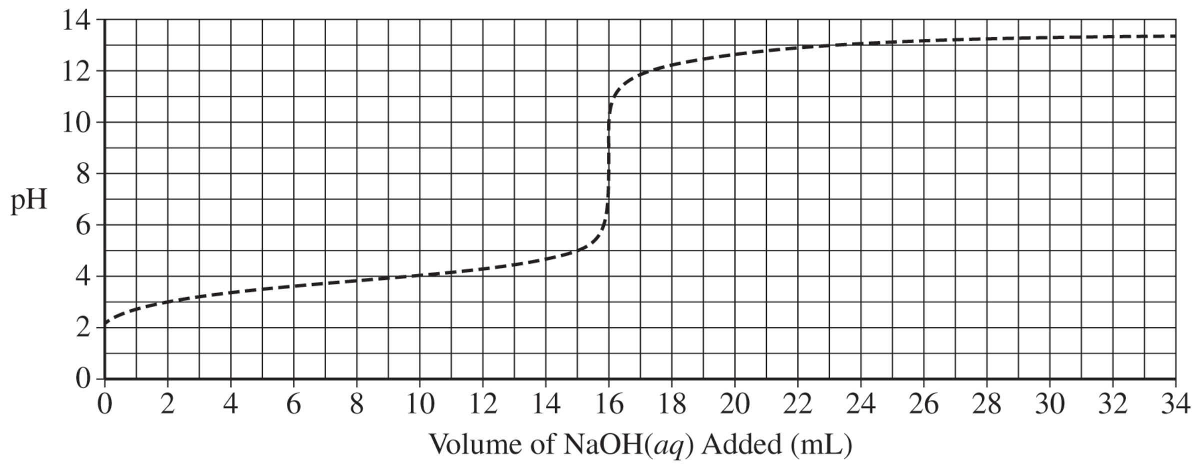
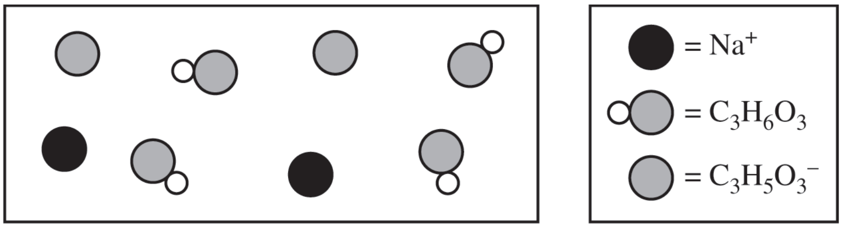
Continue your response to **QUESTION 1** on this page.

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



(c) Use the information in the graph to determine the approximate pK_a of lactic acid. ____________



(d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

(i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.

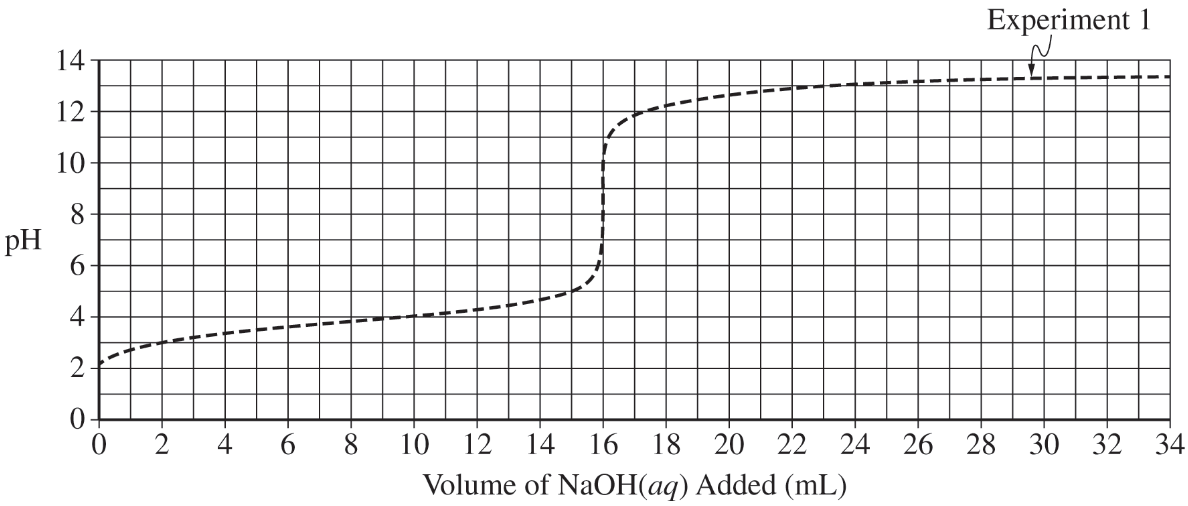
(ii) Justify your answer.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

Experiment	Mass of NaOH(s) (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

(iii) The student repeats the experiment but uses a solution of NaOH(aq) with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



(e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g / mL and that the specific heat capacity of the combined solution is 4.2 J / (g · °C).

(i) Calculate the quantity of heat produced in the reaction, in J.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

(ii) Calculate the molar enthalpy of reaction, in kJ / mol_{rxn}. Include the sign in your answer.

(iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

2. A chemical reaction between maleic acid ($H_2C_4H_2O_4$) and sodium bicarbonate ($NaHCO_3$) occurs in the presence of water to produce carbon dioxide and sodium maleate ($Na_2C_4H_2O_4$), as represented by the following equation.

$$H_2C_4H_2O_4(aq) + 2\,NaHCO_3(aq) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) + Na_2C_4H_2O_4(aq)$$

(a) A student combines equal masses of $H_2C_4H_2O_4(s)$ chunks and $NaHCO_3(s)$ chunks with sufficient water at 20.0°C. The student determines that 0.0114 mol of $CO_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $CO_2(g)$ produced.

(ii) The $CO_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm. Calculate the volume of $CO_2(g)$, in liters.

(b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $H_2C_4H_2O_4(s)$ and $NaHCO_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

(iii) When the reaction is complete, will the volume of $CO_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $H_2C_4H_2O_4$ (grams)	Mass of $NaHCO_3$ (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

(c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

(d) The reaction has a value of $\Delta S°$ greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

(e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S^\circ_{rxn} > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.

$$H_2C_4H_2O_4 + H_2O \rightleftarrows HC_4H_2O_4^{\,-} + H_3O^+ \qquad K_{a_1} = 1.5 \times 10^{-2}$$

$$HC_4H_2O_4^{\,-} + H_2O \rightleftarrows C_4H_2O_4^{\,2-} + H_3O^+ \qquad K_{a_2} = 8.5 \times 10^{-7}$$

(f) Calculate the pK_{a_2} value for the $HC_4H_2O_4^{\,-}$ ion.

(g) A buffer solution with a pH of 7.00 is prepared using $C_4H_2O_4^{\,2-}$ and $HC_4H_2O_4^{\,-}$. Calculate the ratio $\frac{[C_4H_2O_4^{\,2-}]}{[HC_4H_2O_4^{\,-}]}$ in this solution.

GO ON TO THE NEXT PAGE.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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

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

1. A student reacts 0.300 g of methyl salicylate ($C_8H_8O_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($HC_7H_5O_3$).

(a) For every 1 mole of $C_8H_8O_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($HC_7H_5O_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $HC_7H_5O_3$ that could be produced in this reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

As part of the experimental procedure to purify the $HC_7H_5O_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $HC_7H_5O_3$ are given in the following table.

Properties of Salicylic Acid ($HC_7H_5O_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $HC_7H_5O_3$. The student suggests that some of the $HC_7H_5O_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $HC_7H_5O_3$ (molar mass 138.12 g / mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

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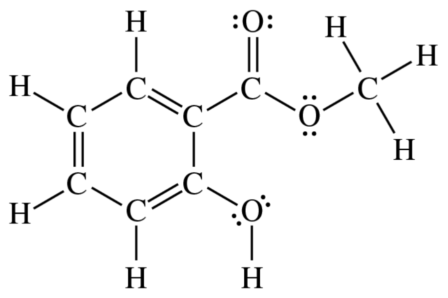
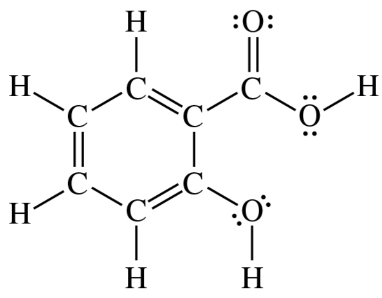
Continue your response to **QUESTION 1** on this page.

The structures and melting points for methyl salicylate and salicylic acid are shown.



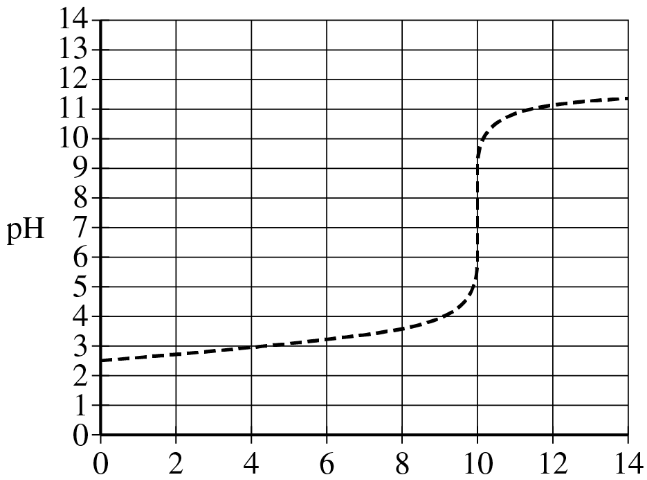
Methyl Salicylate
Melting Point: –9°C



Salicylic Acid
Melting Point: 159°C

(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $HC_7H_5O_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



Volume of 0.0200 M NaOH Added (mL)

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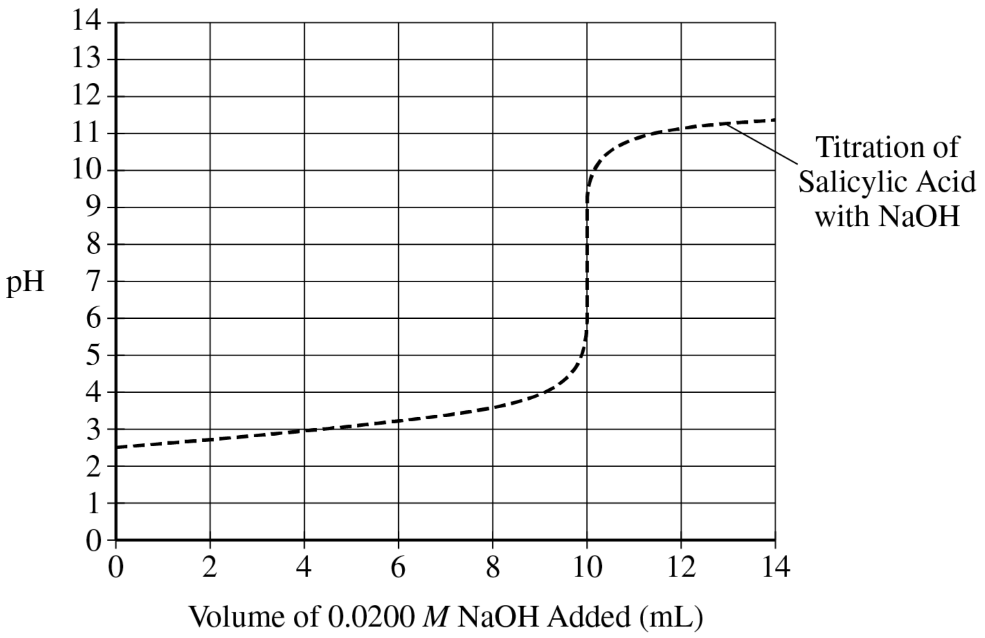
Continue your response to **QUESTION 1** on this page.

(e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. ______________

(f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.

(g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5}. Calculate the value of pK_a for benzoic acid.

(h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 M benzoic acid solution with 0.0200 M NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 M salicylic acid. The initial pH of the benzoic acid solution is 3.11.



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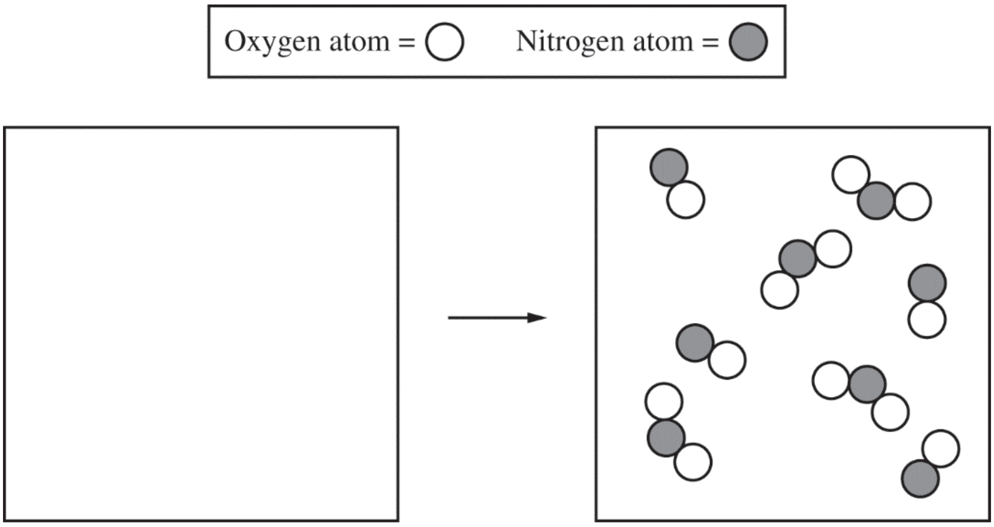
$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

   (a) The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $NO(g)$ and $O_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



Reactant Mixture   Product Mixture

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
-40.4 kJ/mol$_{rxn}$	-138.5 J/(K·mol$_{rxn}$)	0.87 kJ/mol$_{rxn}$

   (b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

      (i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

      (ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

   (c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$N_2O_3(g)$ reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

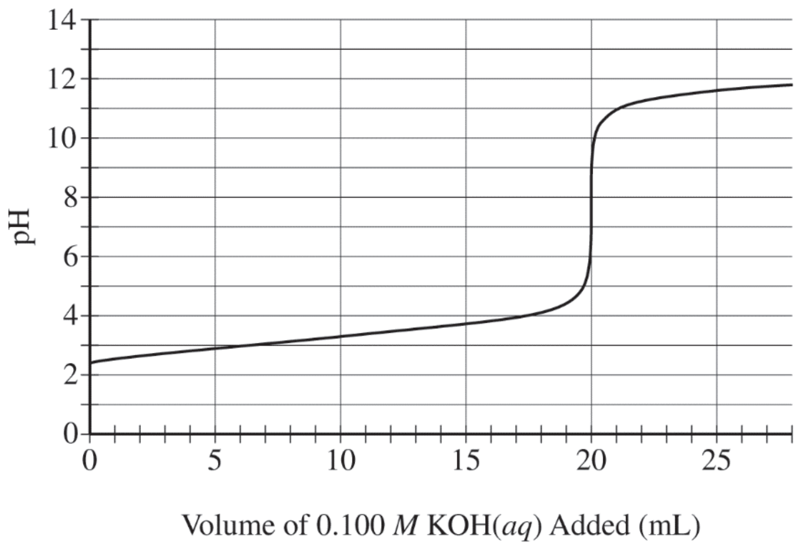
H O N O

(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

To produce an aqueous solution of HNO_2, the student bubbles $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 *M* KOH(*aq*). The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The following titration curve shows the change in pH of the solution during the titration.



(e) Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

(ii) estimate the value of pK_a for $HNO_2(aq)$

(f) During the titration, after a volume of 15 mL of 0.100 *M* KOH(*aq*) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

$$C_6H_5OH(aq) + H_2O(l) \rightleftarrows C_6H_5O^-(aq) + H_3O^+(aq) \qquad K_a = 1.12 \times 10^{-10}$$

4. Phenol is a weak acid that partially dissociates in water according to the equation above.

   (a) What is the pH of a 0.75 M $C_6H_5OH(aq)$ solution?

   (b) For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle <u>each</u> pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

1 2 3 4 5 6 7 8 9 10 11 12 13 14

8.8 Properties of Buffers

Name: ______________ Class: __________ Date: ____________ **Total: 9 marks**

KEY WORDS acid 酸 • buffer 缓冲溶液 • ph pH 值 • base 碱 • conjugate base 共轭碱

Objective

Build the skills to answer exam questions on the **properties of buffers**.

You must be able to:

- explain why a buffer works best when $[HA] \approx [A^-]$
- state that a buffer's pH is near its pK_a
- choose an acid for a target buffer pH

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ A buffer's pH is near its pKa

A buffer's pH is set by the acid's pK_a and the ratio of base to acid. When $[A^-] = [HA]$, the ratio is 1 and $pH = pK_a$.

■ Best buffering near pKa

A buffer resists change best when it has **plenty of both** members and they are **comparable** in amount — near a 1:1 ratio, i.e. near $pH = pK_a$.

■ Choosing the acid

To make a buffer at a target pH, pick a weak acid whose pK_a is **close to** that pH (within about ± 1). For a pH-5 buffer, choose an acid with $pK_a \approx 5$ (like acetic acid, $pK_a = 4.7$).

■ Range

A buffer is effective roughly within $pK_a \pm 1$; outside that range one component is nearly used up.

2 Practice

Now apply the methods above.

2.1 When $[HA] = [A^-]$, the pH equals what? [1]

2.2 To make a buffer at pH 9, what pK_a should the acid have? [1]

2.3 Over what pH range is a buffer effective? [1]

3 Exam-style questions

3.1 A buffer works best when the acid and its conjugate base are [1]

- **A** in very different amounts
- **B** in comparable amounts
- **C** both absent
- **D** both strong

3.2 You need a buffer at pH 4.5. Available acids: formic (p$K_a = 3.7$), acetic (p$K_a = 4.7$), and hypochlorous (p$K_a = 7.5$).

(a) Which is the best choice? [1]

(b) Justify your choice. [2]

3.3 Explain why a buffer loses its effectiveness far from its pK_a. [2]

Solutions

2.1 pK_a.

2.2 About 9.

2.3 Roughly p$K_a \pm 1$.

3.1 **B** — comparable amounts.

3.2 (a) Acetic acid. (b) Its p$K_a = 4.7$ is closest to the target pH 4.5 (within ± 1), so the acid and base are in comparable amounts and buffer effectively.

3.3 Far from pK_a the ratio $[A^-]/[HA]$ is extreme, so one component is nearly depleted and cannot neutralize added acid or base — buffering fails.

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

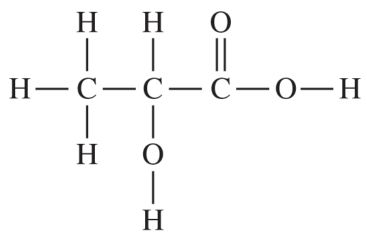
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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

$$C_3H_6O_3(aq) + NaOH(aq) \rightarrow NaC_3H_5O_3(aq) + H_2O(l)$$

1. A student is studying the reaction between lactic acid, $C_3H_6O_3$, and sodium hydroxide, NaOH, as represented in the balanced equation above.

(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.

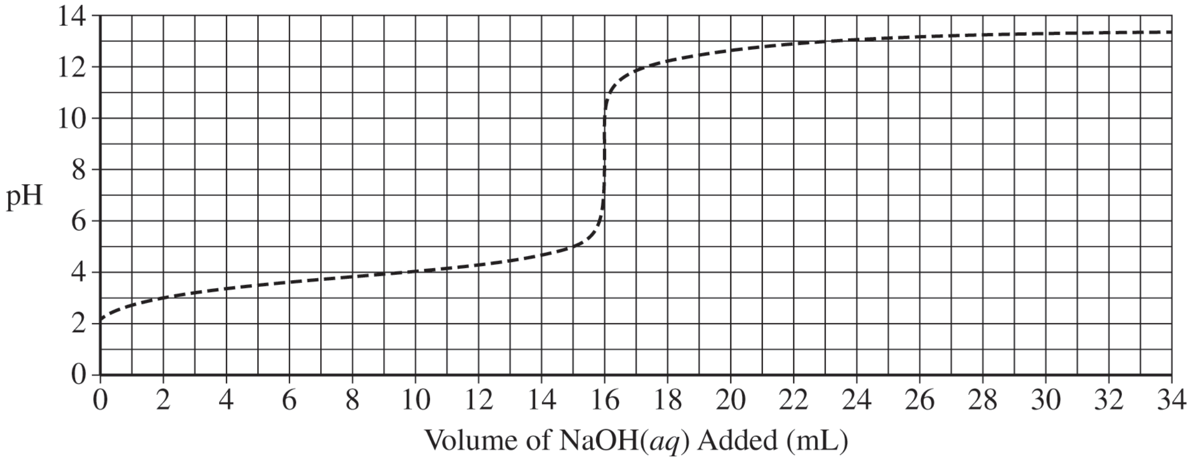


(b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g / mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

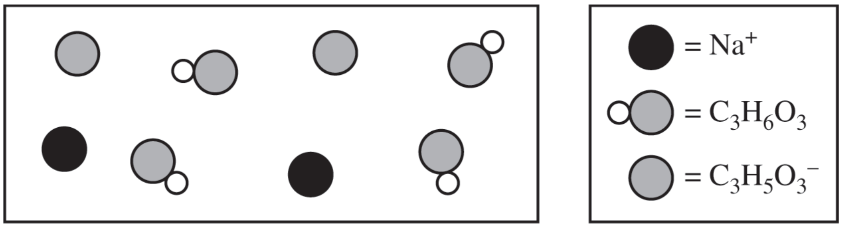
GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



(c) Use the information in the graph to determine the approximate pK_a of lactic acid. ____________



(d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

(i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.

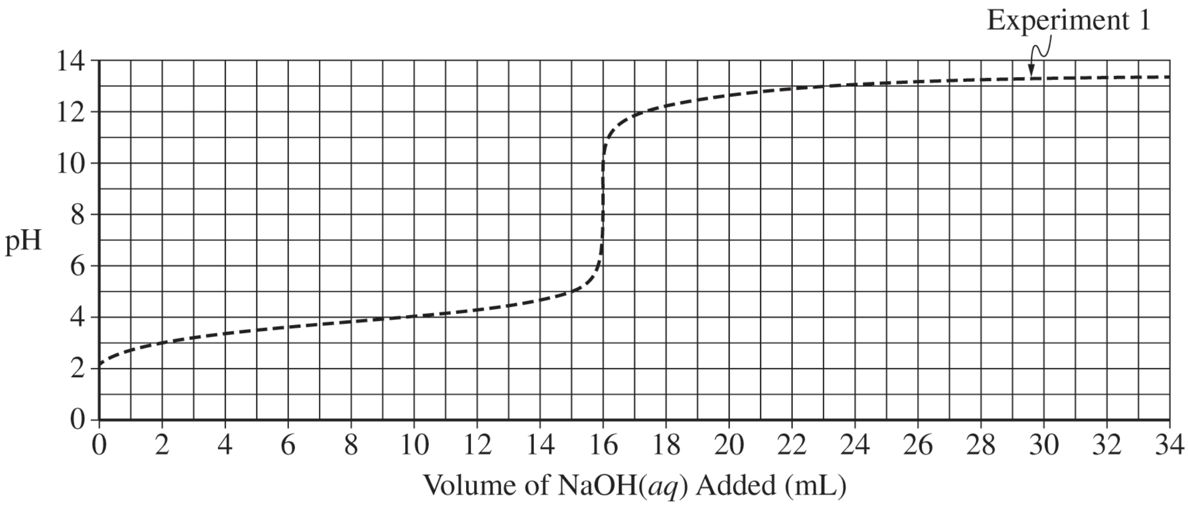
(ii) Justify your answer.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

Experiment	Mass of NaOH(s) (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

(iii) The student repeats the experiment but uses a solution of NaOH(aq) with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



(e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g / mL and that the specific heat capacity of the combined solution is 4.2 J / (g · °C).

(i) Calculate the quantity of heat produced in the reaction, in J.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

(ii) Calculate the molar enthalpy of reaction, in kJ / mol_{rxn}. Include the sign in your answer.

(iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

8.9 The Henderson-Hasselbalch Equation

Name: ______________ Class: __________ Date: ____________ **Total: 12 marks**

KEY WORDS ph pH 值 • buffer 缓冲溶液 • acid 酸 • base 碱

Objective

Build the skills to answer exam questions on the **Henderson-Hasselbalch equation**.

You must be able to:

- use $pH = pK_a + \log \frac{[A^-]}{[HA]}$
- find a buffer's pH from the ratio
- find the ratio needed for a target pH

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

- **The equation**

$$pH = pK_a + \log \frac{[A^-]}{[HA]}.$$

It gives a buffer's pH from the base-to-acid ratio.

- **Equal amounts**

When $[A^-] = [HA]$, the log term is $\log 1 = 0$, so $pH = pK_a$.

- **A worked pH**

A buffer with $pK_a = 4.7$, $[A^-] = 0.20$, $[HA] = 0.10$:

$$pH = 4.7 + \log \frac{0.20}{0.10} = 4.7 + \log 2 = 4.7 + 0.30 = 5.0.$$

- **Finding the ratio for a target pH**

Rearrange: $\log \frac{[A^-]}{[HA]} = pH - pK_a$, then take $10^{(pH - pK_a)}$.

2 Practice

Now apply the methods above.

2.1 Write the Henderson-Hasselbalch equation. [1]

2.2 A buffer has $pK_a = 4.7$ with equal acid and base. Find the pH. [1]

2.3 Find the pH of a buffer with $pK_a = 5.0$ and $\frac{[A^-]}{[HA]} = 10$. [2]

3 Exam-style questions

3.1 When $[A^-] = [HA]$, the Henderson-Hasselbalch equation gives pH = [1]

- **A** 0
- **B** 7
- **C** pK_a
- **D** $pK_a + 1$

3.2 A buffer uses an acid with $pK_a = 4.74$, with $[HA] = 0.30$ M and $[A^-] = 0.15$ M.

(a) Find the ratio $\frac{[A^-]}{[HA]}$. [1]

(b) Find the pH. [3]

3.3 You want a buffer at pH 5.0 using an acid with $pK_a = 4.7$. Find the required ratio

$\dfrac{[A^-]}{[HA]}$. [3]

Solutions

2.1 $\mathrm{pH} = \mathrm{p}K_a + \log \dfrac{[\mathrm{A}^-]}{[\mathrm{HA}]}$.

2.2 $\mathrm{pH} = 4.7$.

2.3 $\mathrm{pH} = 5.0 + \log 10 = 5.0 + 1 = 6.0$.

3.1 **C** — $\mathrm{pH} = \mathrm{p}K_a$.

3.2 (a) $\dfrac{0.15}{0.30} = 0.5$. (b) $\mathrm{pH} = 4.74 + \log(0.5) = 4.74 - 0.30 = 4.44$.

3.3 $\log \dfrac{[\mathrm{A}^-]}{[\mathrm{HA}]} = 5.0 - 4.7 = 0.3$; ratio $= 10^{0.3} = 2.0$.

Question 3: Version J

The following information applies to all parts.

---

3. Nitrous acid, HNO_2, is a weak acid that ionizes according to Equation 1.

$$\text{Equation 1: } HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq) \quad K_a = 5.6\times10^{-4} \text{ at } 298\text{ K}$$

Part A

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $HNO_2(aq)$ with an initial concentration of $0.125\ M$ has a pH of 2.09.

i. **Calculate** the value of $[H_3O^+]$ in the solution. Show the work that leads to your answer.

ii. **Calculate** $[HNO_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of $0.125\ M$ $HNO_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[HNO_2] = 0.114\ M$, $[NO_2^-] = 0.0109\ M$, and $[H_3O^+] = 0.0109\ M$.

i. **Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.

ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

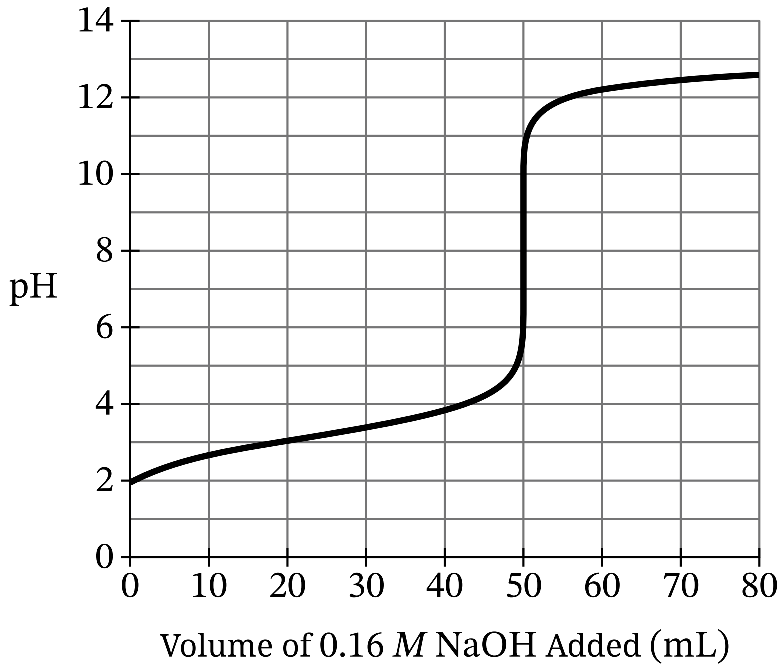
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $HNO_2(aq)$ in the bottle, the student titrates 35.0 mL of the $HNO_2(aq)$ with 0.16 *M* $NaOH(aq)$ at 298 K, which reacts according to Equation 2.

$$\text{Equation 2: } HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $HNO_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[HNO_2] > [NO_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a; the autoionization of water, K_w; and the neutralization reaction represented by Equation 2, K_2.

Table 1

Chemical Equation	Equilibrium Constant
$HNO_2(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $HNO_2(aq)$ solution and titrating the solution with 0.16 M $NaOH(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O.

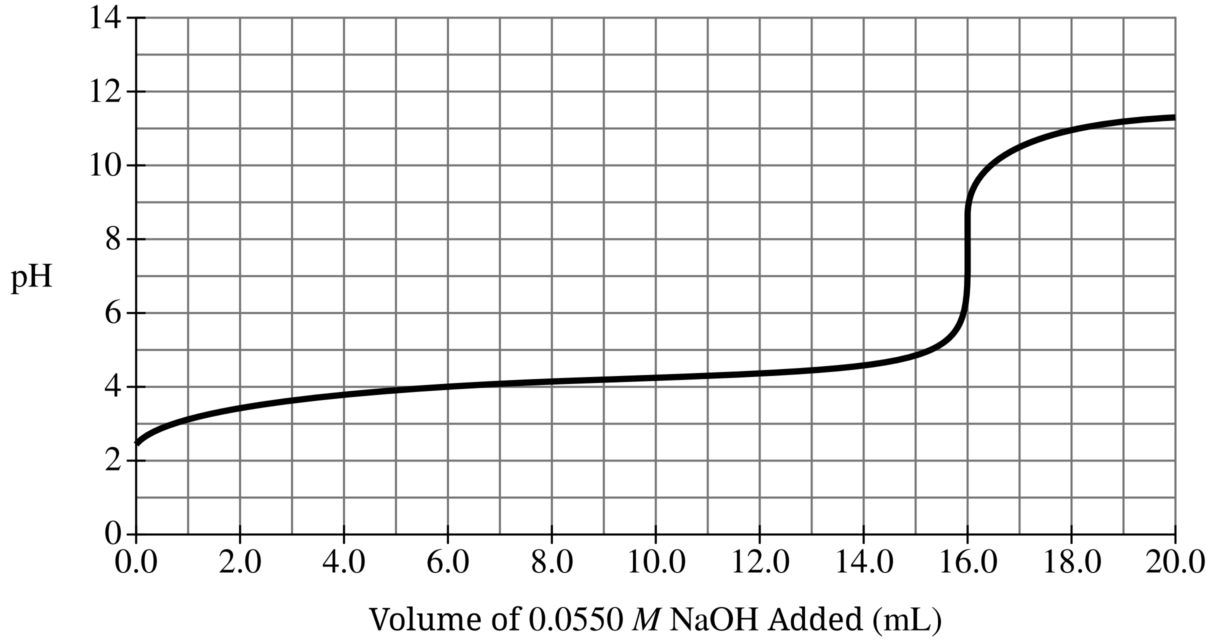
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $\mathrm{HAsc}(aq)$, acts as a weak acid, as shown in the equation.

$$\mathrm{HAsc}(aq) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{Asc^-}(aq)$$

The following titration curve was produced when a 10.0 mL sample of $\mathrm{HAsc}(aq)$ was titrated using 0.0550 M $\mathrm{NaOH}(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate $\mathrm{p}K_a$ of ascorbic acid.

iii. What is the value of the ratio $\dfrac{[\mathrm{Asc^-}]}{[\mathrm{HAsc}]}$ when the pH of the solution is 4.7?

C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^-, as represented by the following equation.

$$\text{HAsc} + I_3^- \rightarrow \text{DHAsc} + 3\,I^- + 2\,H^+$$

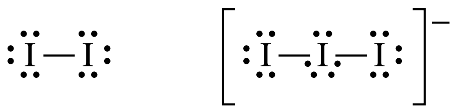
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^-, producing the following data.

Trial	[HAsc] (M)	$[I_3^-]\,(M)$	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

i. The rate law for the reaction is $rate = k[\text{HAsc}][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.

ii. Calculate the value of the rate constant, k, for the reaction. Include units with your answer.

D. The triiodide ion, I_3^-, is significantly more soluble in water than elemental iodine, I_2, is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



I_2 $\qquad$ I_3^-

2. A chemical reaction between maleic acid ($H_2C_4H_2O_4$) and sodium bicarbonate ($NaHCO_3$) occurs in the presence of water to produce carbon dioxide and sodium maleate ($Na_2C_4H_2O_4$), as represented by the following equation.

$$H_2C_4H_2O_4(aq) + 2\,NaHCO_3(aq) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) + Na_2C_4H_2O_4(aq)$$

(a) A student combines equal masses of $H_2C_4H_2O_4(s)$ chunks and $NaHCO_3(s)$ chunks with sufficient water at 20.0°C. The student determines that 0.0114 mol of $CO_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $CO_2(g)$ produced.

(ii) The $CO_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm. Calculate the volume of $CO_2(g)$, in liters.

(b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $H_2C_4H_2O_4(s)$ and $NaHCO_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

(iii) When the reaction is complete, will the volume of $CO_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $H_2C_4H_2O_4$ (grams)	Mass of $NaHCO_3$ (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

(c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

(d) The reaction has a value of $\Delta S°$ greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

(e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S^\circ_{rxn} > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.

$$H_2C_4H_2O_4 + H_2O \rightleftarrows HC_4H_2O_4^- + H_3O^+ \qquad K_{a_1} = 1.5 \times 10^{-2}$$

$$HC_4H_2O_4^- + H_2O \rightleftarrows C_4H_2O_4^{2-} + H_3O^+ \qquad K_{a_2} = 8.5 \times 10^{-7}$$

(f) Calculate the pK_{a_2} value for the $HC_4H_2O_4^-$ ion.

(g) A buffer solution with a pH of 7.00 is prepared using $C_4H_2O_4^{2-}$ and $HC_4H_2O_4^-$. Calculate the ratio $\dfrac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^-]}$ in this solution.

GO ON TO THE NEXT PAGE.

. A student is asked to prepare a buffer solution made with equimolar amounts of $CH_3NH_2(aq)$ and $CH_3NH_3Cl(s)$. The student uses 25.00 mL of 0.100 M $CH_3NH_2(aq)$, which contains 0.00250 mol of CH_3NH_2, to make the buffer.

(a) Calculate the mass of $CH_3NH_3Cl(s)$ that contains 0.00250 mol of CH_3NH_3Cl.

The student has the following materials and equipment available.

- Distilled water
- Electronic balance
- 50 mL beaker
- Pipets
- 0.100 M $CH_3NH_2(aq)$
- Weighing paper
- 10.0 mL graduated cylinder
- pH meter
- Solid CH_3NH_3Cl
- 50.00 mL buret
- Small spatula

(b) The following table contains a partial procedure for making the buffer solution. Fill in steps 1 and 4 to complete the procedure using only materials and equipment selected from the choices given. (Not all materials listed will be used. Assume that all appropriate safety measures are already in place.)

Step	Procedure
1	
2	Place the solid in the 50 mL beaker.
3	Clean the buret and rinse with distilled water.
4	
5	Use the buret to add 25.00 mL of 0.100 M $CH_3NH_2(aq)$ to the beaker.
6	Mix well.
7	Check the pH with the pH meter.

GO ON TO THE NEXT PAGE.

The value of K_b for $CH_3NH_2(aq)$ is 4.4×10^{-4}, and the pH of the buffer the student prepared is 10.64.

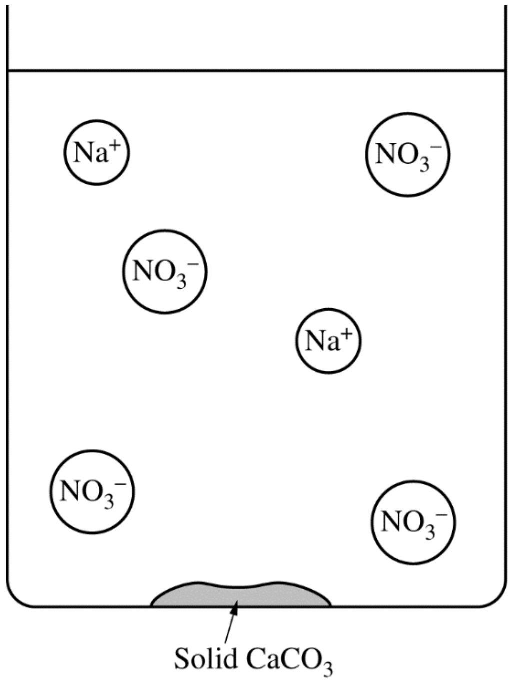
(c) The student prepares a second buffer solution. The student uses 25.00 mL of 0.050 M $CH_3NH_2(aq)$ instead of 25.00 mL of 0.100 M $CH_3NH_2(aq)$, and half the mass of $CH_3NH_3Cl(s)$ that was used in the first buffer. Is the pH of the second buffer greater than, less than, or equal to the pH of the first buffer? Justify your answer.

3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 *M* $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

$$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

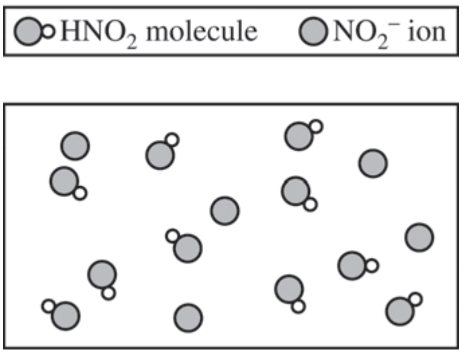
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 M $NaOH(aq)$ the student should add to 100. mL of 0.100 M $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 M $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



3. Potassium sorbate, $KC_6H_7O_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $KC_6H_7O_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M HCl(aq) using both an indicator and a pH meter. The value of K_a for sorbic acid, $HC_6H_7O_2$, is 1.7×10^{-5}.

(a) Write the net-ionic equation for the reaction between $KC_6H_7O_2(aq)$ and HCl(aq).

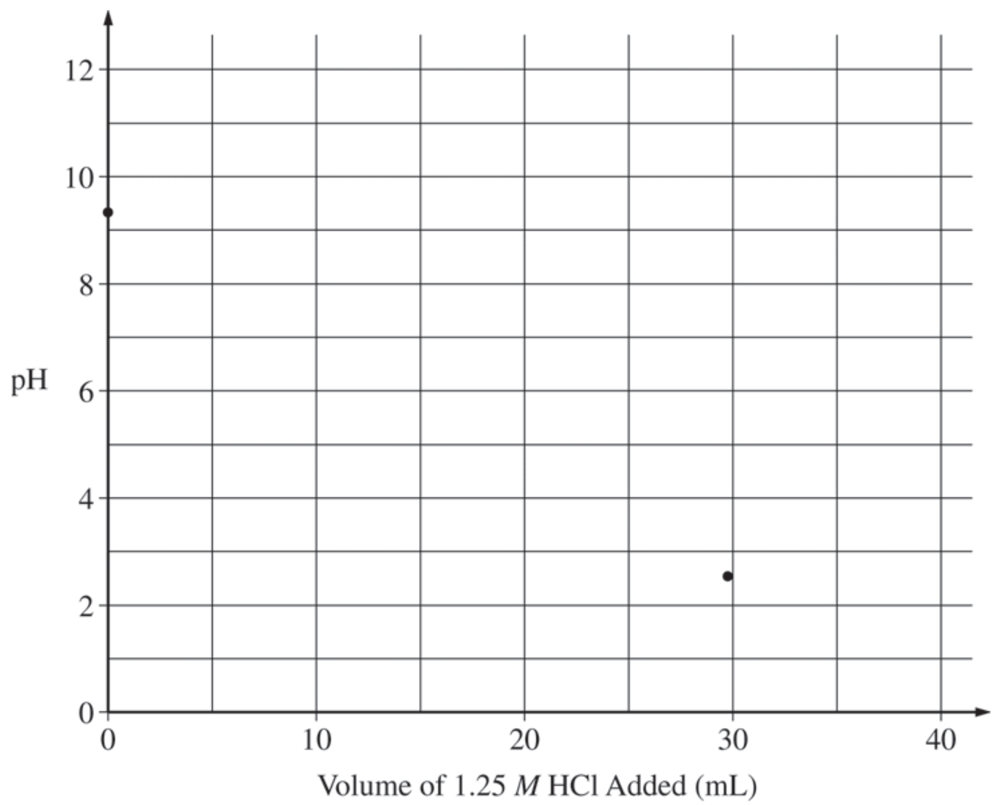
(b) A total of 29.95 mL of 1.25 M HCl(aq) is required to reach the equivalence point. Calculate $[KC_6H_7O_2]$ in the stock solution.

(c) The pH at the equivalence point of the titration is measured to be 2.54 Which of the following indicators would be the best choice for determining the end point of the titration? Justify your answer.

Indicator	pK_a
Phenolphthalein	9.3
Bromothymol blue	7.0
Methyl red	5.0
Thymol blue	2.0
Methyl violet	0.80

(d) Calculate the pH at the half-equivalence point.

(e) The initial pH and the equivalence point are plotted on the graph below. Accurately sketch the titration curve on the graph below. Mark the position of the half-equivalence point on the curve with an X.



(f) The pH of the soft drink is 3.37 after the addition of the $KC_6H_7O_2(aq)$. Which species, $HC_6H_7O_2$ or $C_6H_7O_2^-$, has a higher concentration in the soft drink? Justify your answer.

8.10 Buffer Capacity

Name: ______________ Class: __________ Date: ____________ **Total: 9 marks**

KEY WORDS buffer capacity 缓冲容量 • buffer 缓冲溶液 • acid 酸 • base 碱 • ph pH 值

Objective

Build the skills to answer exam questions on **buffer capacity**.

You must be able to:

- define **buffer capacity 缓冲容量** (how much acid/base a buffer absorbs)
- link capacity to the **amounts** of the buffer components
- compare two buffers' capacities

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Buffer capacity

Buffer capacity is how much added acid or base a buffer can neutralize before its pH changes significantly. It depends on the **amounts** (moles) of the weak acid and its conjugate base.

■ More moles, more capacity

A **concentrated** buffer (more moles of both components) has a **larger** capacity than a dilute one with the same ratio — same pH, but it can absorb more.

■ Ratio vs capacity

The **ratio** sets the **pH**; the **amounts** set the **capacity**. Two buffers can have the same pH but very different capacities.

■ Best capacity near 1:1

Capacity is greatest when $[A^-] \approx [HA]$ (near $pH = pK_a$), because there is plenty of both to react with either added acid or base.

2 Practice

Now apply the methods above.

2.1 What does buffer capacity measure? [1]

2.2 Which sets the pH: the ratio or the amounts? [1]

2.3 Two buffers have the same ratio but one is more concentrated. Which has the greater capacity? [1]

3 Exam-style questions

3.1 Buffer capacity depends mainly on the [1]

- **A** ratio of base to acid
- **B** amounts (moles) of the components
- **C** temperature only
- **D** color

3.2 Buffer P is 1.0 M acid + 1.0 M base; buffer Q is 0.10 M acid + 0.10 M base (same pK_a).

(a) Compare their pH. [1]

(b) Compare their buffer capacities, with a reason. [2]

3.3 Explain why a buffer has its greatest capacity when $[A^-] \approx [HA]$. [2]

Solutions

2.1 How much added acid or base it can neutralize before the pH changes much.

2.2 The ratio sets the pH.

2.3 The more concentrated one.

3.1 **B** — the amounts (moles) of the components.

3.2 (a) Same pH (same ratio and pK_a). (b) Buffer P has the greater capacity — more moles of both components, so it can absorb more added acid or base.

3.3 With comparable amounts of both, there is plenty of conjugate base to neutralize added acid **and** plenty of weak acid to neutralize added base, so it resists change in either direction most effectively.

$$N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

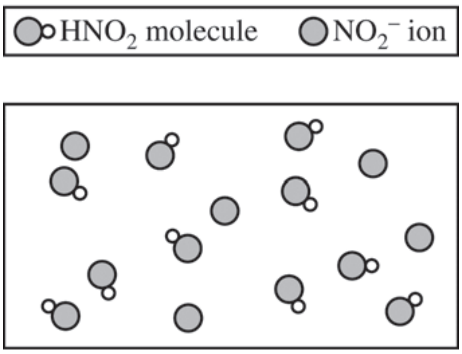
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 *M* $HNO_2(aq)$ and 0.100 *M* $NaOH(aq)$.

(i) Explain why the addition of 0.100 *M* $NaOH(aq)$ to 0.100 *M* $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 *M* $NaOH(aq)$ the student should add to 100. mL of 0.100 *M* $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 *M* $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



AP CHEMISTRY • EXERCISE SHEET

8.11 pH and Solubility

Name: ______________ Class: __________ Date: ____________ **Total: 9 marks**

KEY WORDS ph pH 值 • acid 酸 • conjugate base 共轭碱 • weak acid 弱酸 • base 碱

Objective

Build the skills to answer exam questions on **pH and solubility** — how acid affects solubility.

You must be able to:

- explain why salts of **weak-acid anions** dissolve more in acid
- use Le Chatelier on the solubility equilibrium
- predict the effect of lowering pH

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

Acid dissolves basic-anion salts

If a salt's anion is the conjugate base of a **weak acid** (e.g. CO_3^{2-}, F^-, OH^-), adding acid removes that anion (it reacts with H^+), so **more** salt dissolves.

The Le Chatelier view

$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$. Add H^+: it consumes CO_3^{2-} (forming HCO_3^-/H_2CO_3), so the equilibrium shifts **right** — more solid dissolves.

No effect for strong-acid anions

Salts whose anion is from a **strong** acid (e.g. Cl^-, NO_3^-) are **not** affected by pH — those anions do not react with H^+.

A worked prediction

$Mg(OH)_2$ dissolves more in acid: H^+ removes OH^-, shifting the dissolution right. AgCl is unaffected by pH (Cl^- is a spectator).

2 Practice

Now apply the methods above.

2.1 Does adding acid increase the solubility of $CaCO_3$? [1]

2.2 Why is AgCl solubility unaffected by pH? [1]

2.3 Adding H^+ to a hydroxide salt removes which ion? [1]

3 Exam-style questions

3.1 Lowering the pH increases the solubility of a salt whose anion is [1]

- **A** the conjugate base of a weak acid
- **B** from a strong acid
- **C** a metal
- **D** always insoluble

3.2 Consider $CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$. Acid is added.

(a) State the effect on solubility. [1]

(b) Explain using Le Chatelier's principle (note F^- is a weak-acid anion). [2]

3.3 Explain why NaCl solubility does not change with pH but $Mg(OH)_2$ does. [2]

Solutions

2.1 Yes.

2.2 Cl^- is the anion of a strong acid, so it does not react with H^+.

2.3 OH^-.

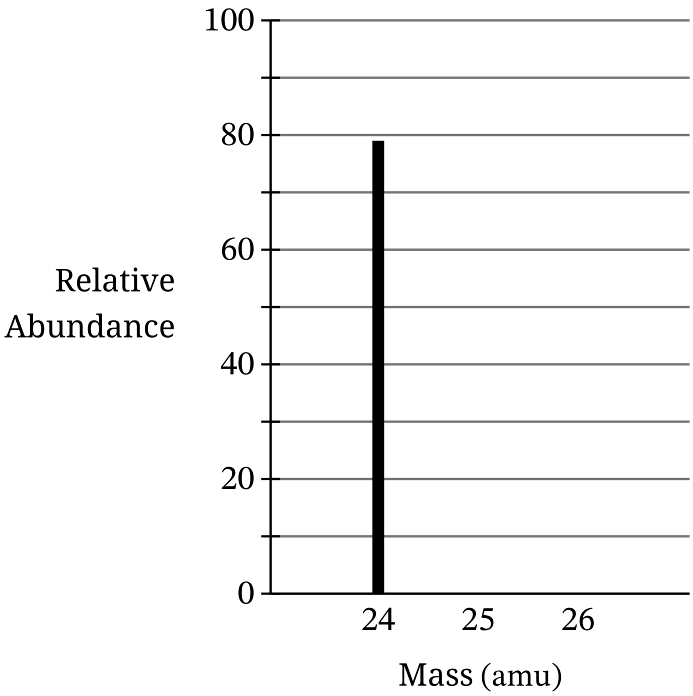
3.1 **A** — the conjugate base of a weak acid.

3.2 (a) It increases. (b) H^+ reacts with F^- to form HF, removing F^-; the equilibrium shifts right to replace it, dissolving more CaF_2.

3.3 Cl^- is a strong-acid anion that does not react with H^+, so pH has no effect; OH^- reacts with H^+, so lowering pH dissolves more $Mg(OH)_2$.

1. Answer the following questions about magnesium.

A. An incomplete mass spectrum for magnesium is shown in the diagram.

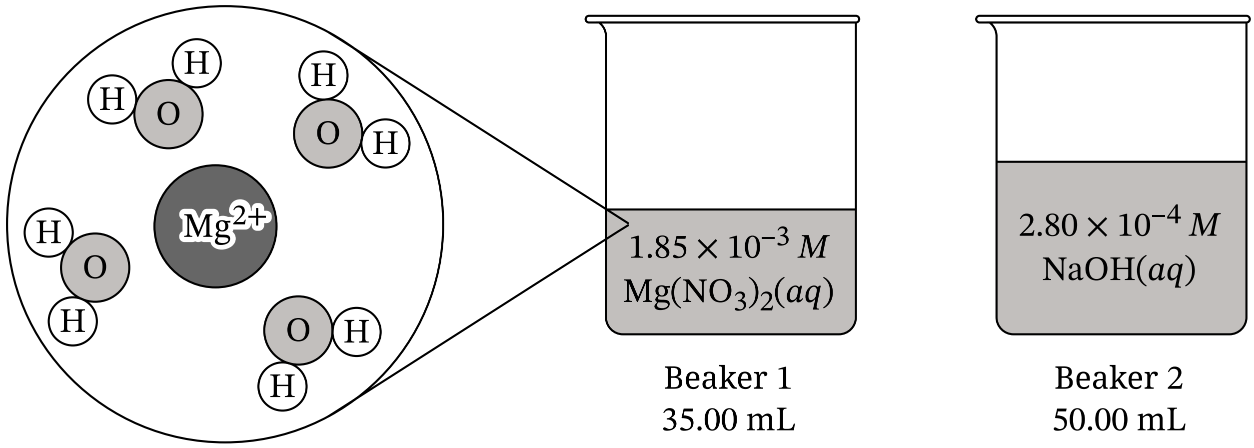


The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.

ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a 1.85×10^{-3} M solution of $Mg(NO_3)_2(aq)$ in beaker 1 and a 2.80×10^{-4} M solution of $NaOH(aq)$ in beaker 2, as shown.



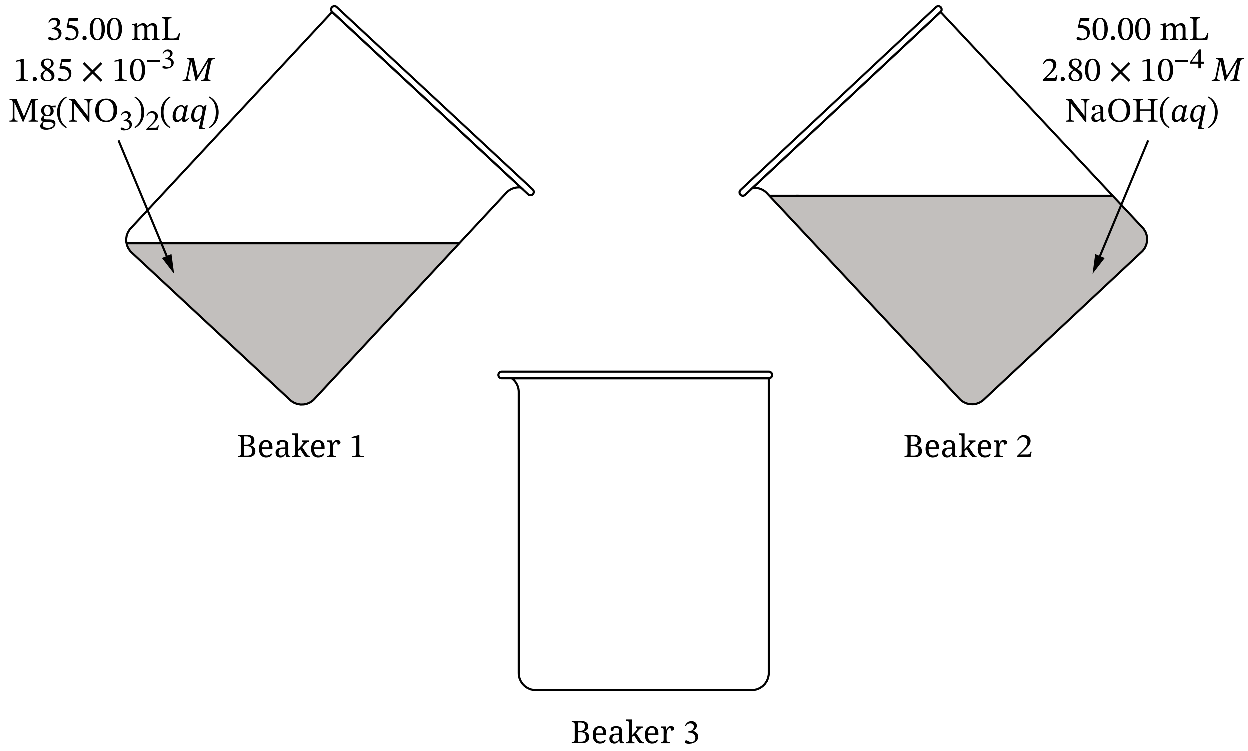
B. The particle diagram shown represents a magnesium ion, Mg^{2+}, in beaker 1. A sodium ion, Na^{+}, in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

i. The relative charge of the ions

ii. The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

D. A student combines 35.00 mL of 1.85×10^{-3} M $Mg(NO_3)_2(aq)$ with 50.00 mL of 2.80×10^{-4} M $NaOH(aq)$, as shown in the diagram. Calculate $[Mg^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



E. The dissolution of magnesium hydroxide is represented by the following equation.

$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq) \qquad K_{sp} = 5.61\times10^{-12}$$

i. Write the expression for the solubility product constant, K_{sp}.

ii. After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[OH^-] = 1.65\times10^{-4}\ M$. Using your answer to part D, calculate the value of the reaction quotient, Q.

iii. Using the reaction quotient, Q, predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.

F. In a separate experiment, the student adds $HNO_3(aq)$ to decrease the pH of a saturated solution containing undissolved $Mg(OH)_2(s)$. Does the amount of undissolved $Mg(OH)_2(s)$ increase, decrease, or remain the same as the $HNO_3(aq)$ is added? Justify your answer.