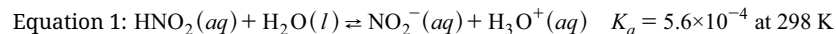


Question 3: Version J

The following information applies to all parts.

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

**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 $\text{HNO}_2(aq)$ with an initial concentration of 0.125 M has a pH of 2.09.

- Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- Calculate** $[\text{HNO}_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of 0.125 M $\text{HNO}_2(aq)$ is heated to 333 K. The new equilibrium concentrations are determined to be $[\text{HNO}_2] = 0.114 \text{ M}$, $[\text{NO}_2^-] = 0.0109 \text{ M}$, and $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- Calculate** the value of K_a for HNO_2 at 333 K. Show the work that leads to your answer.
- Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K.

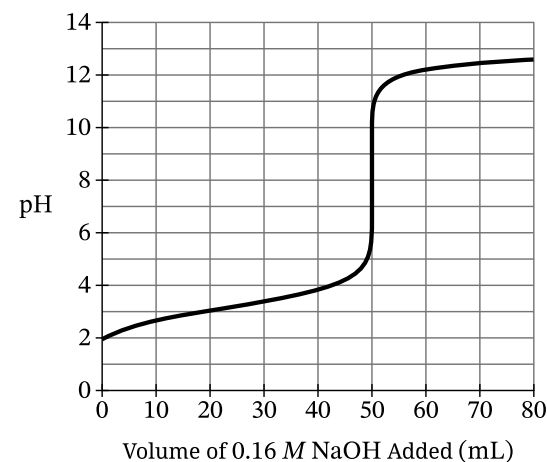
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ in the bottle, the student titrates 35.0 mL of the $\text{HNO}_2(aq)$ with 0.16 M $\text{NaOH}(aq)$ at 298 K, which reacts according to Equation 2.



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 $\text{HNO}_2(aq)$ 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 $[\text{HNO}_2] > [\text{NO}_2^-]$ 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
$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$\text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$	$K_2 = ?$

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

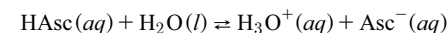
The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

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

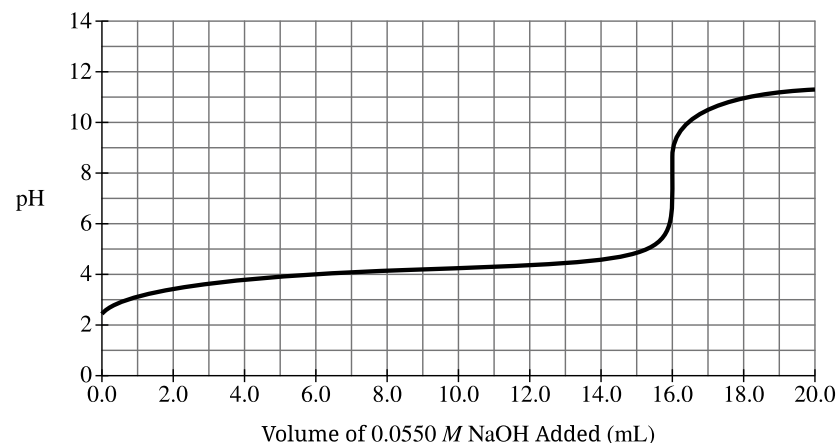
2. Answer the following questions about ascorbic acid (vitamin C).

- A. A student combusts a sample of ascorbic acid, $\text{C}_x\text{H}_y\text{O}_z$, 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 .
- Calculate the number of moles of H_2O produced.
 - 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.



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



- Calculate the molar concentration of the ascorbic acid solution.
- From the titration curve, determine the approximate $\text{p}K_a$ of ascorbic acid.
- What is the value of the ratio $\frac{[\text{Asc}^-]}{[\text{HAsc}]}$ when the pH of the solution is 4.7?

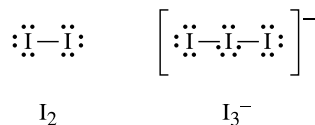
C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.



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

Trial	[HAsc] (M)	$[\text{I}_3^-]$ (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}

- The rate law for the reaction is $\text{rate} = k[\text{HAsc}][\text{I}_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.
 - 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.



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

CHEMISTRY

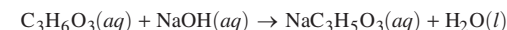
SECTION II

Time—1 hour and 45 minutes

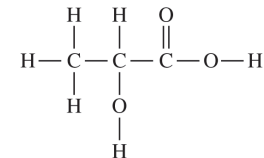
7 Questions

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.



- A student is studying the reaction between lactic acid, $\text{C}_3\text{H}_6\text{O}_3$, and sodium hydroxide, NaOH , as represented in the balanced equation above.
 - 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.

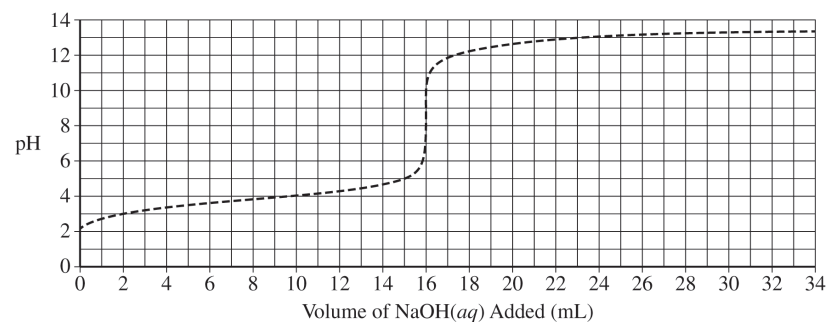


- The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g/mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

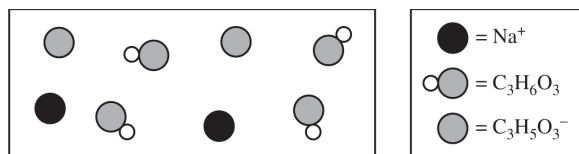
GO ON TO THE NEXT PAGE.

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.)

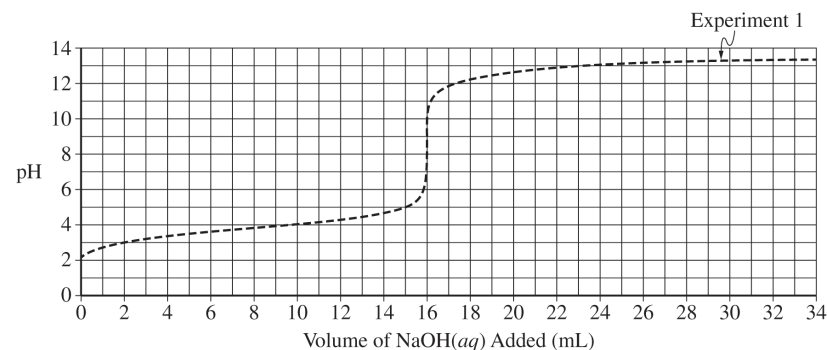
- Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.
- Justify your answer.

GO ON TO THE NEXT PAGE.

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

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

- 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.



- 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).

- 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.

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.

A student reacts 0.300 g of methyl salicylate ($\text{C}_8\text{H}_8\text{O}_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($\text{HC}_7\text{H}_5\text{O}_3$).

(a) For every 1 mole of $\text{C}_8\text{H}_8\text{O}_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($\text{HC}_7\text{H}_5\text{O}_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $\text{HC}_7\text{H}_5\text{O}_3$ 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 $\text{HC}_7\text{H}_5\text{O}_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $\text{HC}_7\text{H}_5\text{O}_3$ are given in the following table.

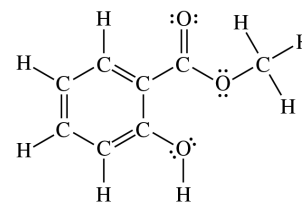
Properties of Salicylic Acid ($\text{HC}_7\text{H}_5\text{O}_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $\text{HC}_7\text{H}_5\text{O}_3$. The student suggests that some of the $\text{HC}_7\text{H}_5\text{O}_3$ 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.

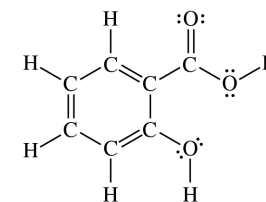
(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $\text{HC}_7\text{H}_5\text{O}_3$ (molar mass 138.12 g/mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

GO ON TO THE NEXT PAGE.Continue your response to **QUESTION 1** on this page.

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



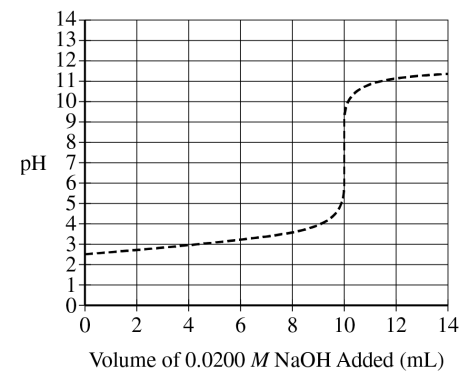
Methyl Salicylate
Melting Point: -9°C



Salicylic Acid
Melting Point: 159°C

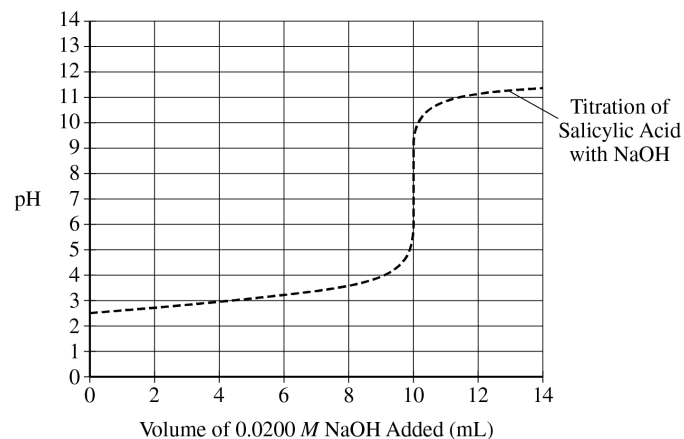
(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $\text{HC}_7\text{H}_5\text{O}_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.

**GO ON TO THE NEXT PAGE.**

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

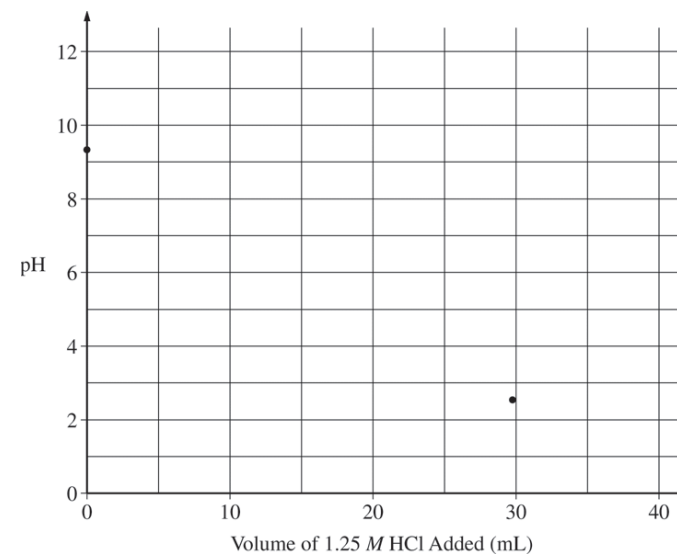
- (e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. _____
- (f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.
- (g) The student researches 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.

**GO ON TO THE NEXT PAGE.**

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.



2. Propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, 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 $\text{CH}_3\text{CH}_2\text{COOH}$ 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 $\text{CH}_3\text{CH}_2\text{COOH}$ 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 $\text{p}K_a$ 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.