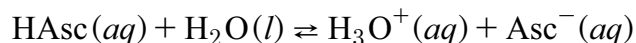


2. Answer the following questions about ascorbic acid (vitamin C).

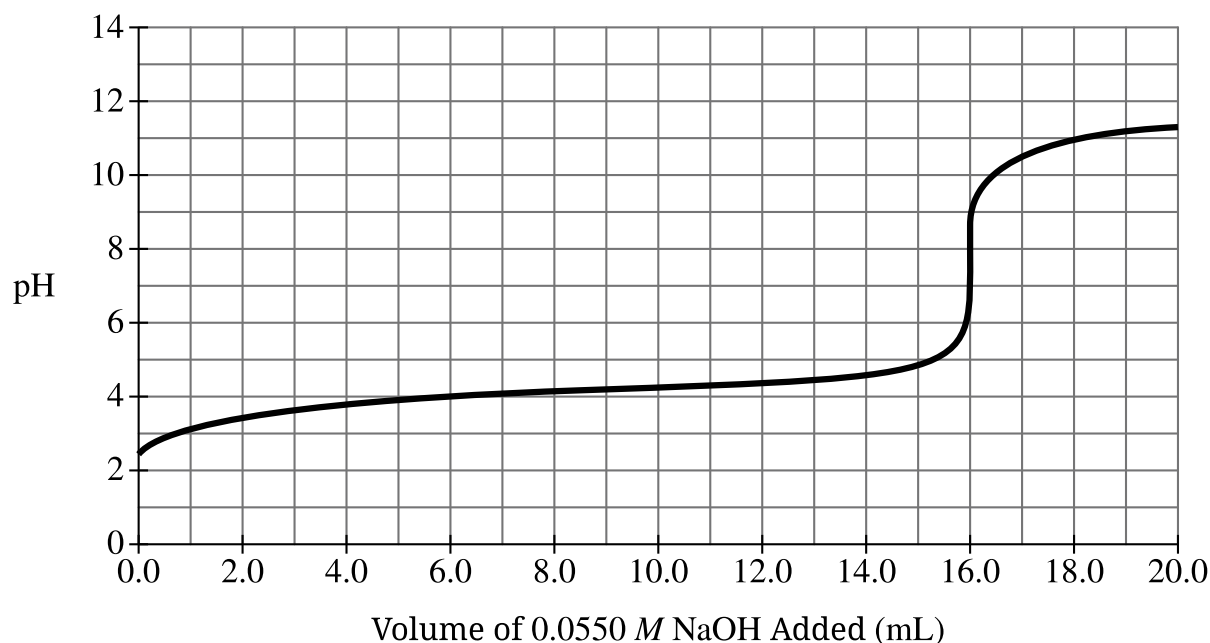
A. A student combusts a sample of ascorbic acid, $C_xH_yO_z$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O .

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



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



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

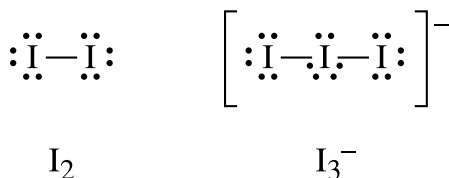
- C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.



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.



A student is asked to prepare a buffer solution made with equimolar amounts of $\text{CH}_3\text{NH}_2(aq)$ and $\text{CH}_3\text{NH}_3\text{Cl}(s)$. The student uses 25.00 mL of 0.100 M $\text{CH}_3\text{NH}_2(aq)$, which contains 0.00250 mol of CH_3NH_2 , to make the buffer.

(a) Calculate the mass of $\text{CH}_3\text{NH}_3\text{Cl}(s)$ that contains 0.00250 mol of $\text{CH}_3\text{NH}_3\text{Cl}$.

The student has the following materials and equipment available.

- | | | | |
|---|----------------------|------------------------------|------------|
| • Distilled water | • Electronic balance | • 50 mL beaker | • Pipets |
| • 0.100 M $\text{CH}_3\text{NH}_2(aq)$ | • Weighing paper | • 10.0 mL graduated cylinder | • pH meter |
| • Solid $\text{CH}_3\text{NH}_3\text{Cl}$ | • 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 $\text{CH}_3\text{NH}_2(aq)$ to the beaker.
6	Mix well.
7	Check the pH with the pH meter.

GO ON TO THE NEXT PAGE.

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

The value of K_b for $\text{CH}_3\text{NH}_2(aq)$ 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 $\text{CH}_3\text{NH}_2(aq)$ instead of 25.00 mL of 0.100 M $\text{CH}_3\text{NH}_2(aq)$, and half the mass of $\text{CH}_3\text{NH}_3\text{Cl}(s)$ 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.**

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.

4. 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	$1.17 \text{ J}/(\text{g}\cdot^\circ\text{C})$
Heat of fusion	27.1 kJ/mol

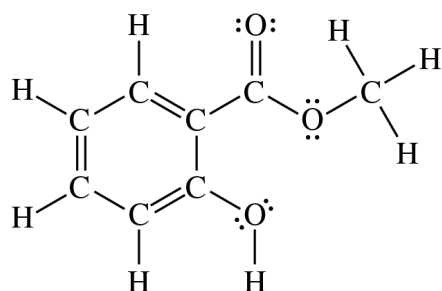
(b) The student's experiment results in an 87% yield of dry $\text{HC}_7\text{H}_5\text{O}_3$. The student suggests that some of the $\text{HC}_7\text{H}_5\text{O}_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield 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.

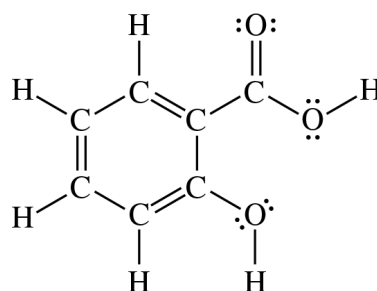
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Continue your response to QUESTION 7 on this page.

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



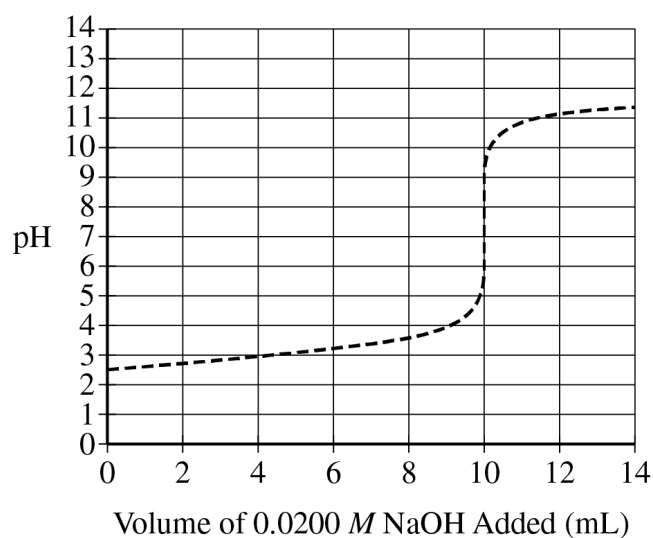
Methyl Salicylate
Melting Point: -9°C



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.

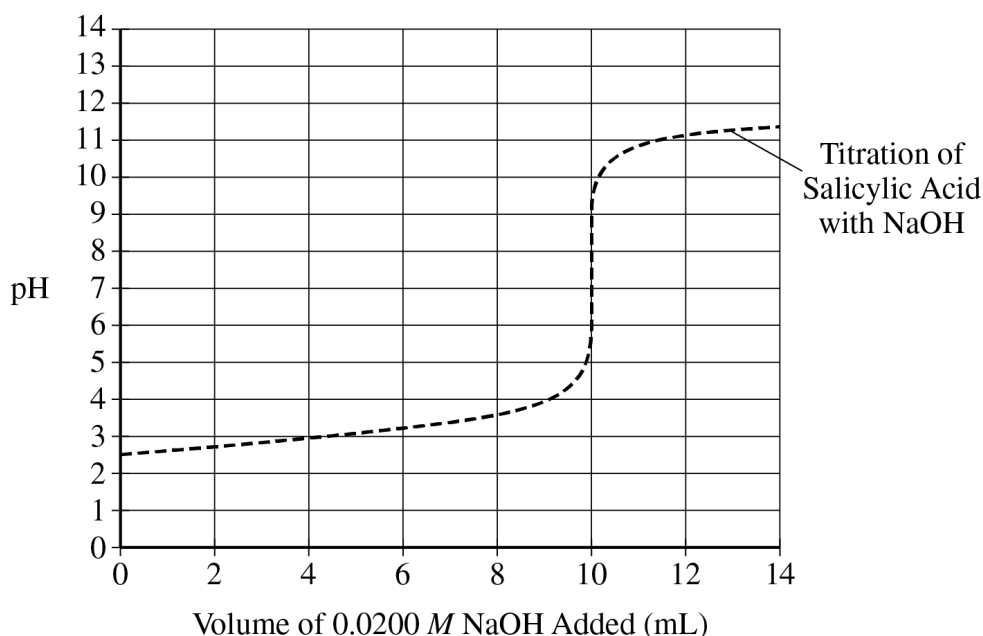
The student titrates 20.0 mL of 0.0100 M $\text{HC}_7\text{H}_5\text{O}_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



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

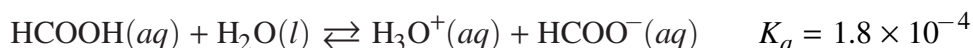
- (e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. _____
- (f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.
- (g) The student researches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

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

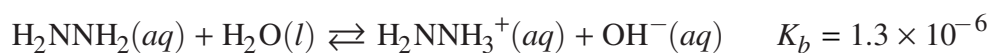
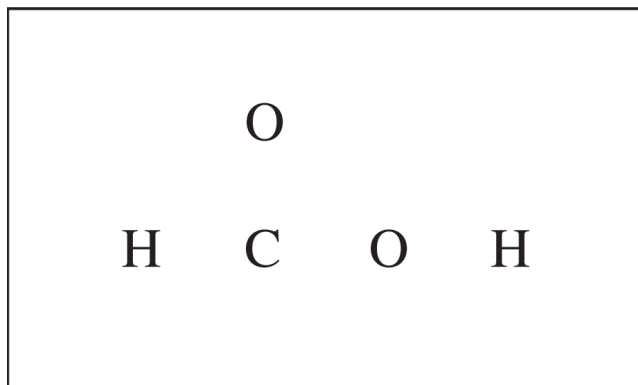
(a) Write the expression for the equilibrium constant, K_a , for the reaction.

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

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

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



(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $\text{H}_2\text{NNH}_2(aq)$ is combined with a 50.0 mL sample of 0.25 M $\text{HCOOH}(aq)$.

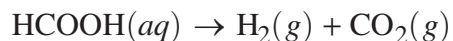
(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH .

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

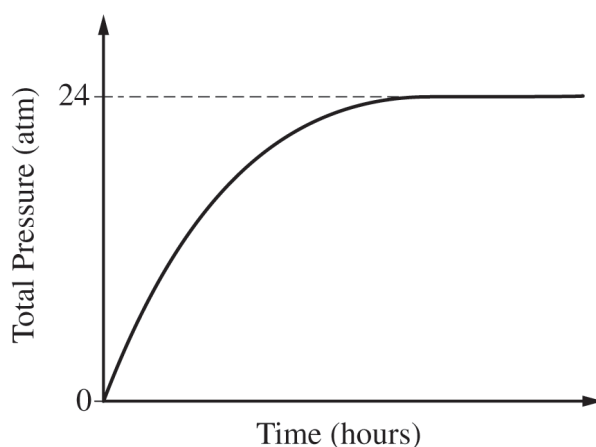
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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

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



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



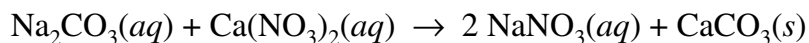
(f) The reaction occurs in a rigid 4.3 L vessel at 25°C , and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $\text{CO}_2(g)$ produced in the reaction. (Assume that the amount of $\text{CO}_2(g)$ dissolved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

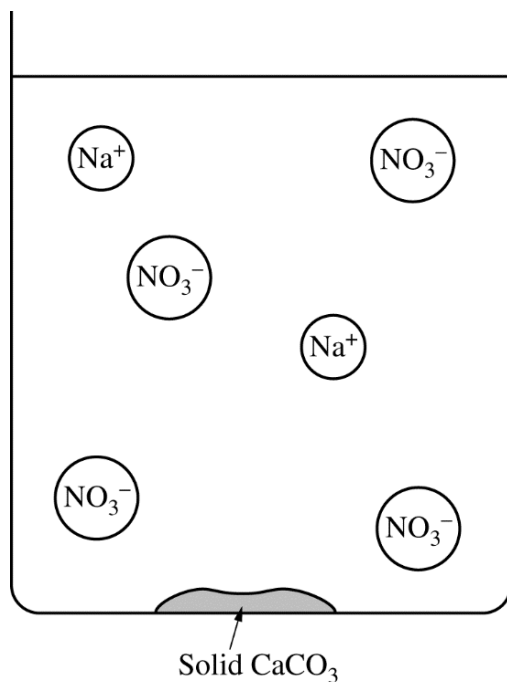
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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

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 $\text{Ca}(\text{NO}_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.



- (a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $\text{Ca}(\text{NO}_3)_2$ 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.

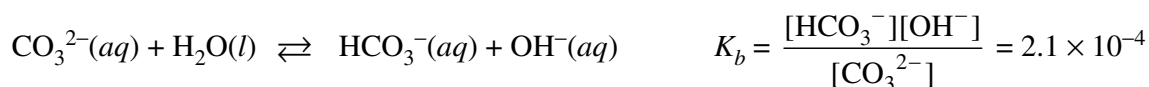


The student filters and dries the precipitate of CaCO_3 (molar mass 100.1 g/mol) and records the data in the table below.

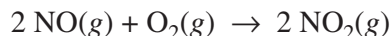
Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $\text{Ca}(\text{NO}_3)_2$ added	100.0 mL
Mass of CaCO_3 precipitate collected	0.93 g

- (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.

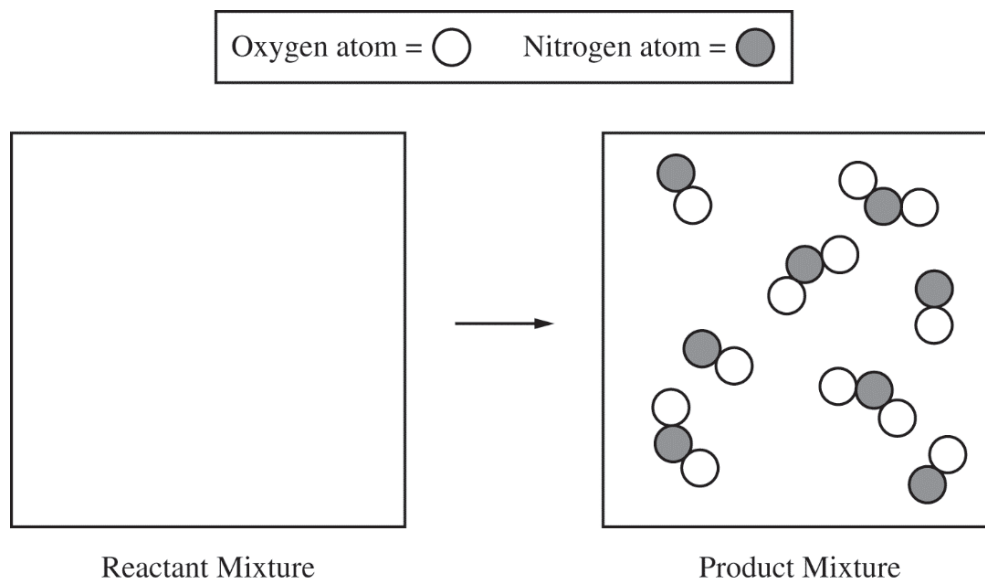
The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $\text{CO}_3^{2-}(aq)$ hydrolyzes to form $\text{HCO}_3^-(aq)$, as shown by the following equation.



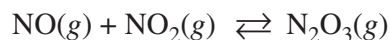
- (f) The student decides to first determine $[\text{OH}^-]$ in the solution, then use that result to calculate the initial concentration of $\text{CO}_3^{2-}(aq)$.
- Identify a laboratory method (not titration) that the student could use to collect data to determine $[\text{OH}^-]$ in the solution.
 - Explain how the student could use the measured value in part (f)(i) to calculate the initial concentration of $\text{CO}_3^{2-}(aq)$. (Do not do any numerical calculations.)
- (g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $\text{HCO}_3^-(aq)$ greater than, less than, or equal to the concentration of $\text{CO}_3^{2-}(aq)$? Justify your answer.
- (h) The student needs to make a $\text{CO}_3^{2-}/\text{HCO}_3^-$ buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.



2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.
- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ 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 $\text{NO}(g)$ and $\text{O}_2(g)$ 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.



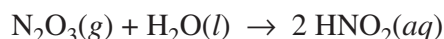
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{\text{rxn}}$	$-138.5 \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$	$0.87 \text{ kJ/mol}_{\text{rxn}}$

- (b) The student begins with an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.
- Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
 - If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.
- (c) The student hypothesizes that increasing the temperature will increase the amount of $\text{N}_2\text{O}_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



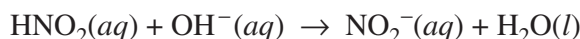
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

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

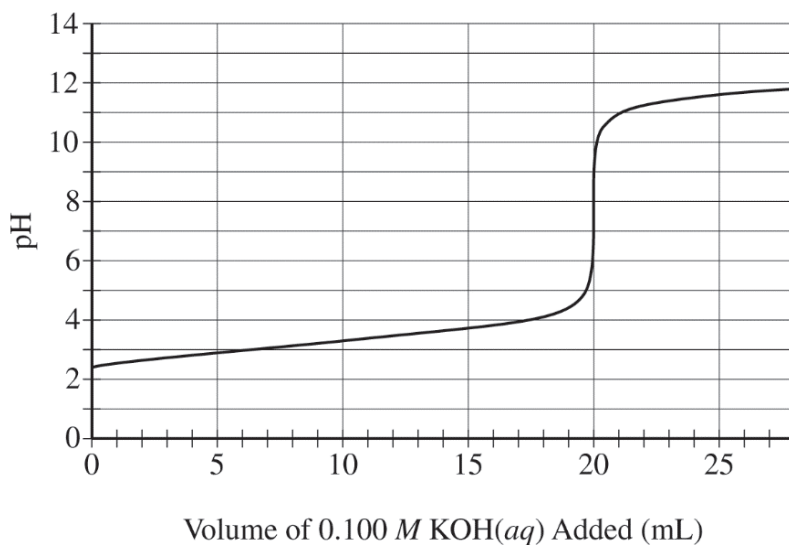


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

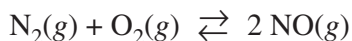
To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



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
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

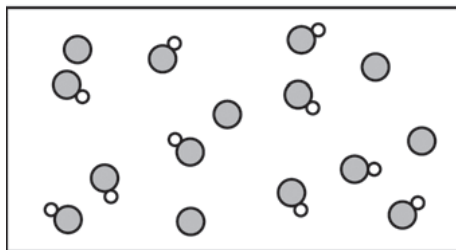
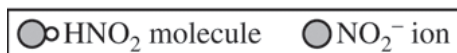


3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

Nitrogen monoxide, $\text{NO}(\text{g})$, 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 $\text{p}K_a$ of 3.40.

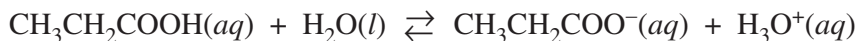
- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.
- (ii) Determine the volume, in mL, of 0.100 M $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ 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 $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. 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 $\text{HNO}_2(\text{aq})$ 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.





2. A student designs an experiment to study the reaction between NaHCO_3 and $\text{HC}_2\text{H}_3\text{O}_2$. 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 $\text{HC}_2\text{H}_3\text{O}_2$. 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 $\text{NaHCO}_3(s)$ and $\text{HC}_2\text{H}_3\text{O}_2(aq)$? 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 ΔG° .
- (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 $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $\text{HNO}_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $\text{HNO}_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.



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.