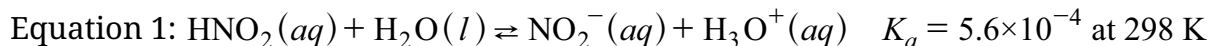


Question 3: Version J

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.

- i. **Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- ii. **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 $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- 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 .

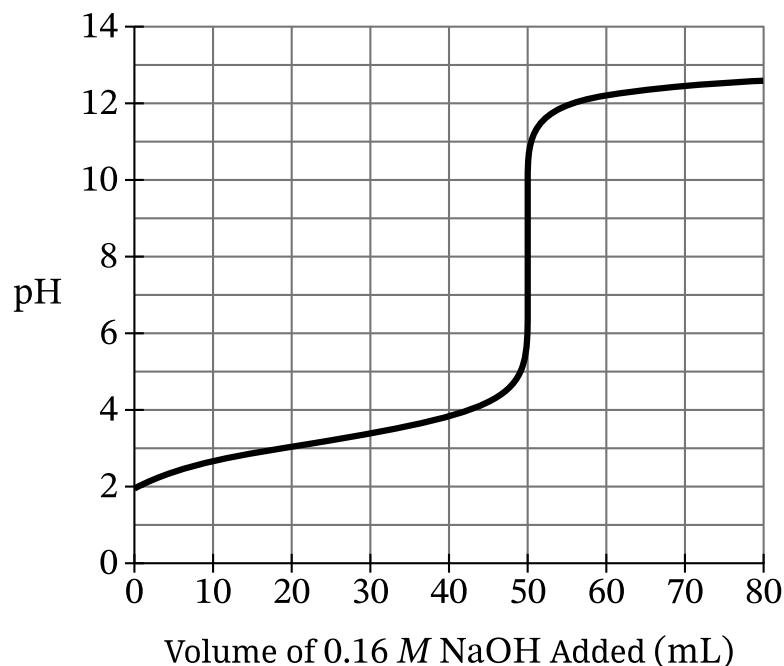
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ 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

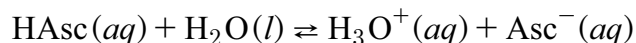
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

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.

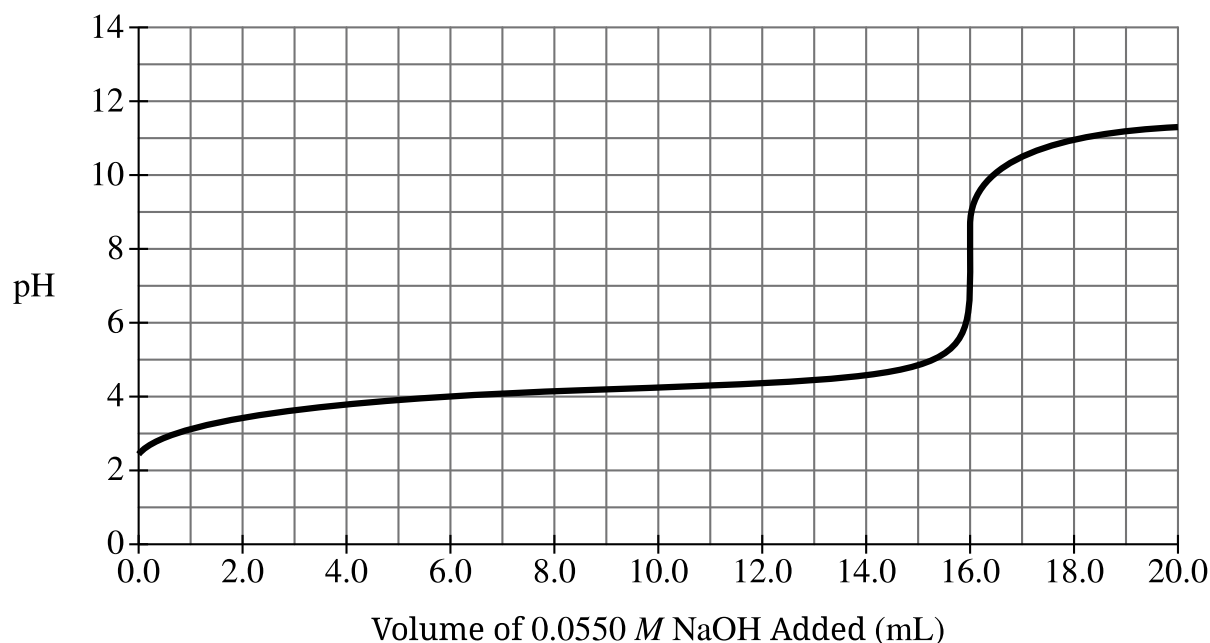
The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

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

- A.** A student combusts a sample of ascorbic acid, $C_xH_yO_z$, 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?

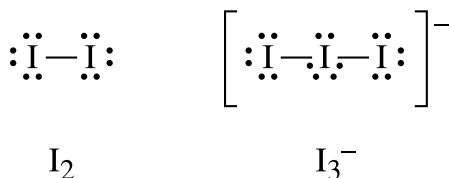
- C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.

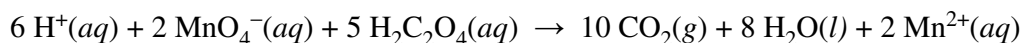


The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^- , producing the following data.

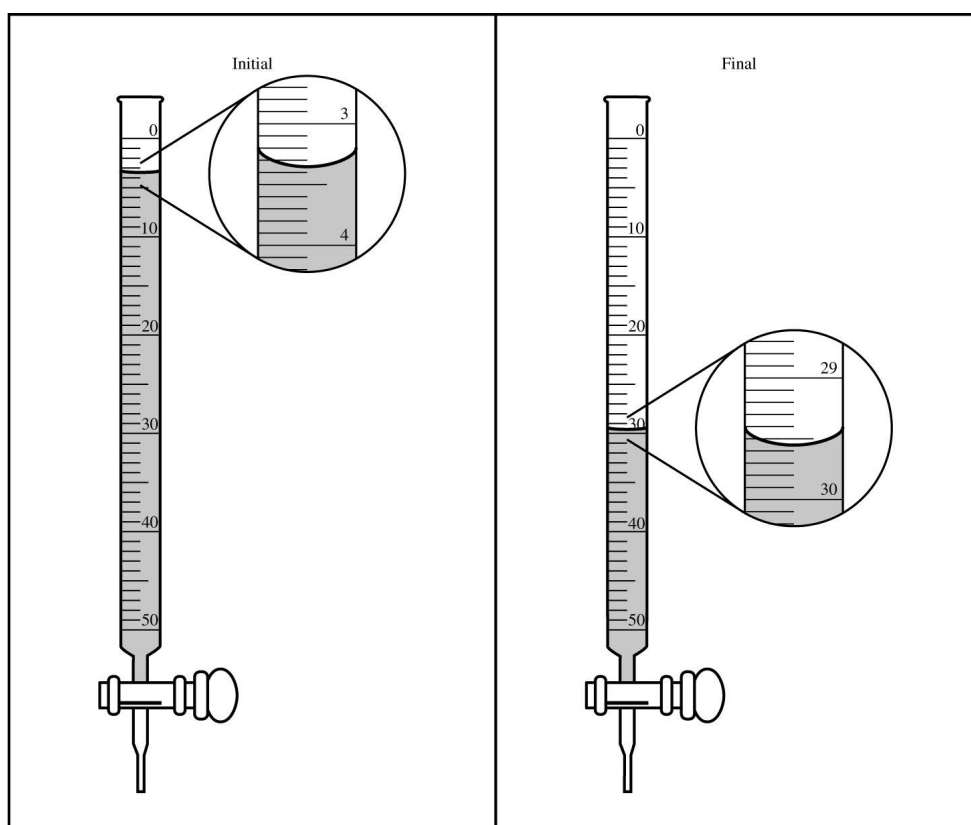
Trial	[HAsc] (M)	$[\text{I}_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

- 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.





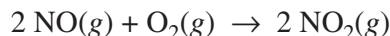
7. A student dissolved a 0.139 g sample of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, in water in an Erlenmeyer flask. Then the student titrated the $\text{H}_2\text{C}_2\text{O}_4$ solution in the flask with a solution of KMnO_4 , which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown above.
- (a) Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.
- (b) The student used a 50.0 mL buret to add the $\text{KMnO}_4(aq)$ to the $\text{H}_2\text{C}_2\text{O}_4(aq)$ until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $\text{KMnO}_4(aq)$ that was added during the titration.



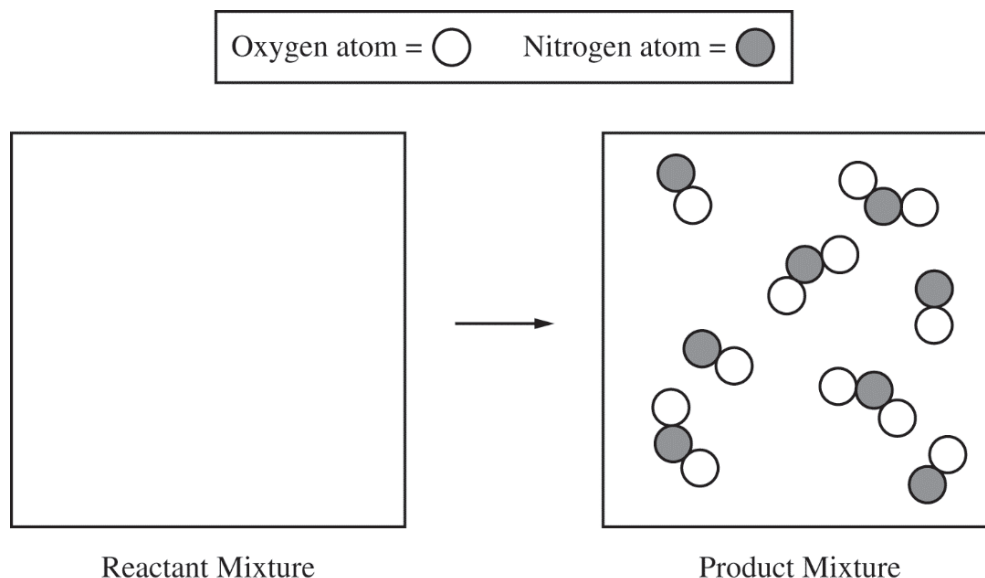
- (c) Given that the concentration of $\text{KMnO}_4(aq)$ was 0.0235 M, calculate the number of moles of MnO_4^- ions that completely reacted with the $\text{H}_2\text{C}_2\text{O}_4$.
- (d) The student proposes to perform another titration using a 0.139 g sample of $\text{H}_2\text{C}_2\text{O}_4$, but this time using 0.00143 M $\text{KMnO}_4(aq)$ in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

STOP

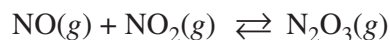
END OF EXAM



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.



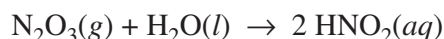
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



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.



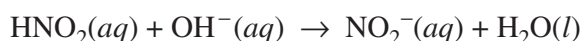
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

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

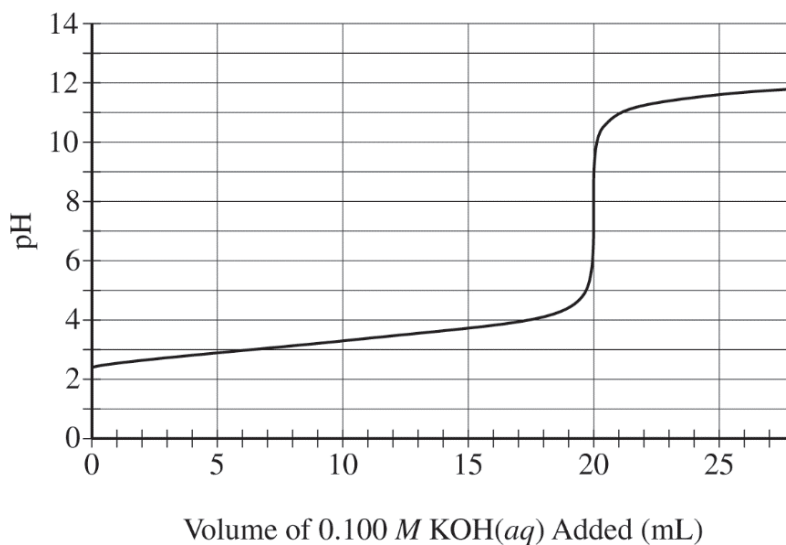


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

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. Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+} .

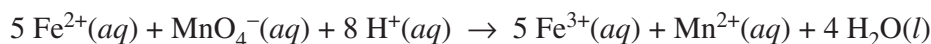
(a) Write the ground-state electron configuration of the Fe^{2+} ion.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

(c) Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

A student obtains a solution that contains an unknown concentration of $\text{Fe}^{2+}(\text{aq})$. To determine the concentration of $\text{Fe}^{2+}(\text{aq})$ in the solution, the student titrates a sample of the solution with $\text{MnO}_4^-(\text{aq})$, which converts $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$, as represented by the following equation.



(d) Write the balanced equation for the half-reaction for the oxidation of $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$.

(e) The student titrates a 10.0 mL sample of the $\text{Fe}^{2+}(\text{aq})$ solution. Calculate the value of $[\text{Fe}^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $\text{KMnO}_4(\text{aq})$ to reach the equivalence point of the titration.

To deliver the 10.0 mL sample of the $\text{Fe}^{2+}(\text{aq})$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

(f) Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $\text{Fe}^{2+}(\text{aq})$ solution.

In a separate experiment, the student is given a sample of powdered $\text{Fe}(\text{s})$ that contains an inert impurity. The student uses a procedure to oxidize the $\text{Fe}(\text{s})$ in the sample to $\text{Fe}_2\text{O}_3(\text{s})$. The student collects the following data during the experiment.

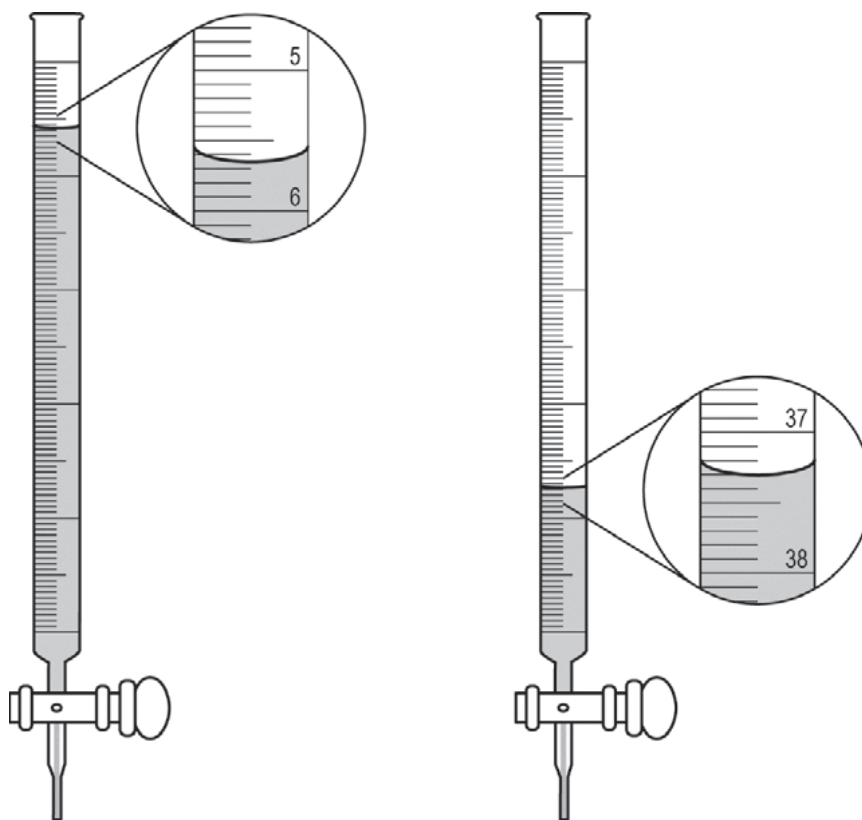
Mass of $\text{Fe}(\text{s})$ with inert impurity	6.724 g
Mass of $\text{Fe}_2\text{O}_3(\text{s})$ produced	7.531 g

(g) Calculate the number of moles of Fe in the $\text{Fe}_2\text{O}_3(\text{s})$ produced.

(h) Calculate the percent by mass of Fe in the original sample of powdered $\text{Fe}(\text{s})$ with the inert impurity.

(i) If the oxidation of the $\text{Fe}(\text{s})$ in the original sample was incomplete so that some of the 7.531 g of product was $\text{FeO}(\text{s})$ instead of $\text{Fe}_2\text{O}_3(\text{s})$, would the calculated mass percent of $\text{Fe}(\text{s})$ in the original sample be higher, lower, or the same as the actual mass percent of $\text{Fe}(\text{s})$? Justify your answer.

7. A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH(aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.
- (a) The images below show the buret before the titration begins (below left) and at the end point (below right). What should the student record as the volume of NaOH(aq) delivered to the flask?



- (b) Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.
- (c) In a second trial, the student accidentally added more NaOH(aq) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculated acid concentration for the second trial? Justify your answer.

STOP

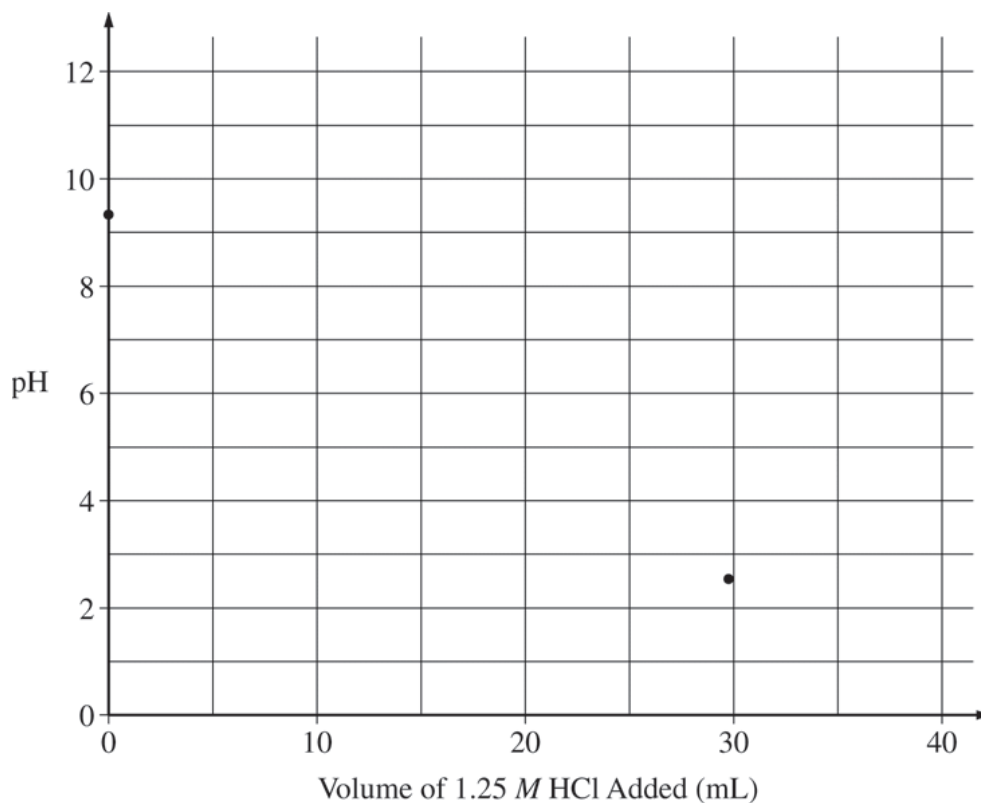
END OF EXAM

3. Potassium sorbate, $\text{KC}_6\text{H}_7\text{O}_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $\text{KC}_6\text{H}_7\text{O}_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M $\text{HCl}(aq)$ using both an indicator and a pH meter. The value of K_a for sorbic acid, $\text{HC}_6\text{H}_7\text{O}_2$, is 1.7×10^{-5} .

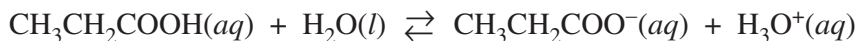
- (a) Write the net-ionic equation for the reaction between $\text{KC}_6\text{H}_7\text{O}_2(aq)$ and $\text{HCl}(aq)$.
- (b) A total of 29.95 mL of 1.25 M $\text{HCl}(aq)$ is required to reach the equivalence point. Calculate $[\text{KC}_6\text{H}_7\text{O}_2]$ in the stock solution.
- (c) The pH at 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	$\text{p}K_a$
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 $\text{KC}_6\text{H}_7\text{O}_2(aq)$. Which species, $\text{HC}_6\text{H}_7\text{O}_2$ or $\text{C}_6\text{H}_7\text{O}_2^-$, 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.