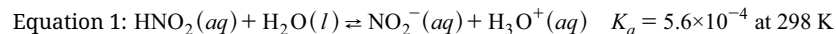


Question 3: Version J

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.

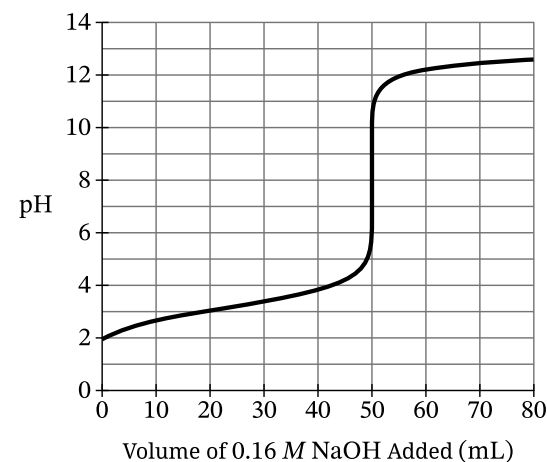
The following information applies to parts D, E, and F.

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

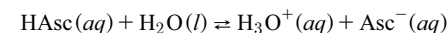
The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

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

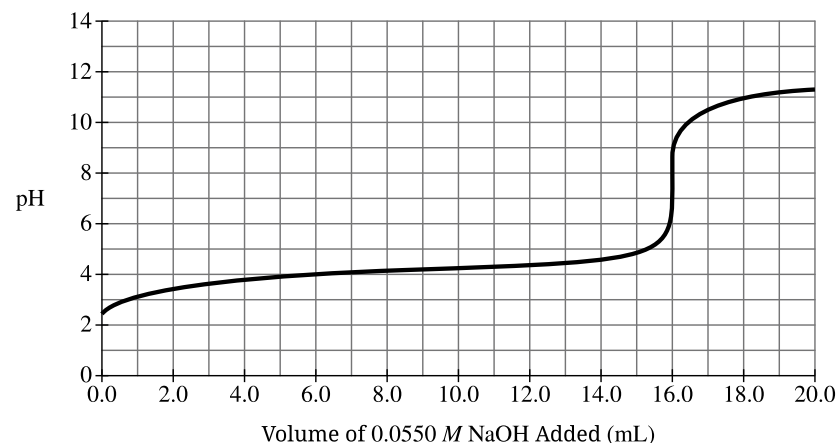
2. Answer the following questions about ascorbic acid (vitamin C).

- 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?

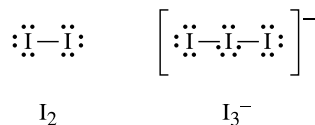
C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.



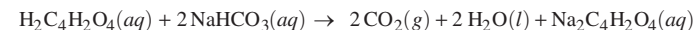
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^- , producing the following data.

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}

- i. 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 $[\text{HAsc}]$.
 - 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.



2. A chemical reaction between maleic acid ($\text{H}_2\text{C}_4\text{H}_2\text{O}_4$) and sodium bicarbonate (NaHCO_3) occurs in the presence of water to produce carbon dioxide and sodium maleate ($\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$), as represented by the following equation.



- (a) A student combines equal masses of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$ chunks and $\text{NaHCO}_3(s)$ chunks with sufficient water at 20.0°C . The student determines that 0.0114 mol of $\text{CO}_2(g)$ is produced after the reaction goes to completion.
 - (i) Calculate the number of grams of $\text{CO}_2(g)$ produced.
 - (ii) The $\text{CO}_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm . Calculate the volume of $\text{CO}_2(g)$, in liters.
- (b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$ and $\text{NaHCO}_3(s)$ 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 $\text{CO}_2(g)$ 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 $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ (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 ΔS° greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

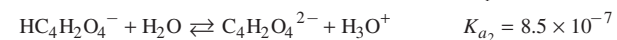
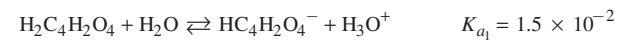
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Continue your response to **QUESTION 2** on this page.

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 $\Delta S_{rxn}^\circ > 0$ 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.



- (f) Calculate the $\text{p}K_{a2}$ value for the $\text{HC}_4\text{H}_2\text{O}_4^-$ ion.

- (g) A buffer solution with a pH of 7.00 is prepared using $\text{C}_4\text{H}_2\text{O}_4^{2-}$ and $\text{HC}_4\text{H}_2\text{O}_4^-$. Calculate the ratio

$$\frac{[\text{C}_4\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_4\text{H}_2\text{O}_4^-]} \text{ in this solution.}$$

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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.

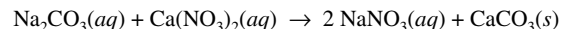
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Continue your response to **QUESTION 4** on this page.

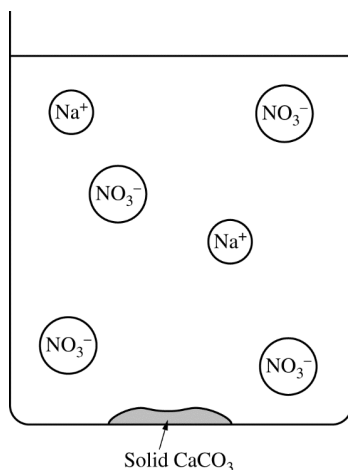
The value of K_b for $\text{CH}_3\text{NH}_2(aq)$ is 4.4×10^{-4} , and the pH of the buffer the student prepared is 10.64.

(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.

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.

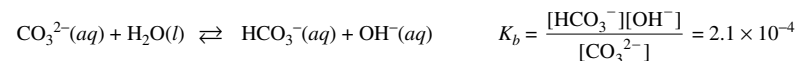


The student filters and dries the precipitate of CaCO_3 (molar mass 100.1 g/mol) and records the data in the table below.

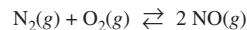
Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $\text{Ca}(\text{NO}_3)_2$ added	100.0 mL
Mass of CaCO_3 precipitate collected	0.93 g

- (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.

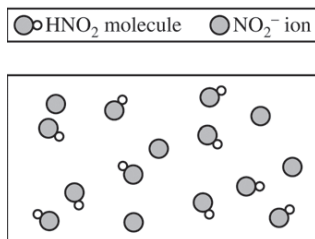
The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $\text{CO}_3^{2-}(aq)$ hydrolyzes to form $\text{HCO}_3^-(aq)$, as shown by the following equation.



- (f) The student decides to first determine $[\text{OH}^-]$ in the solution, then use that result to calculate the initial concentration of $\text{CO}_3^{2-}(aq)$.
- (i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[\text{OH}^-]$ in the solution.
- (ii) 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.



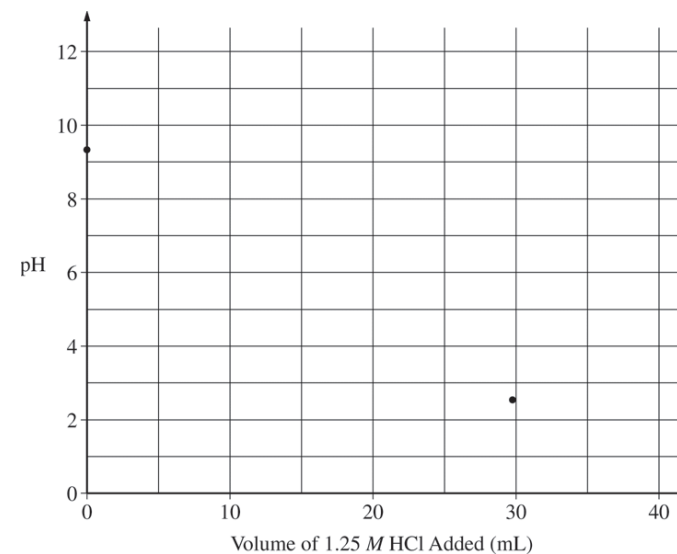
3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.
- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ 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.



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 $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M $\text{HCl}(\text{aq})$ 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 $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$ and $\text{HCl}(\text{aq})$.
- (b) A total of 29.95 mL of 1.25 M $\text{HCl}(\text{aq})$ 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 $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$. 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.