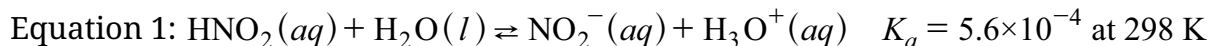


Question 3: Version J

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 .

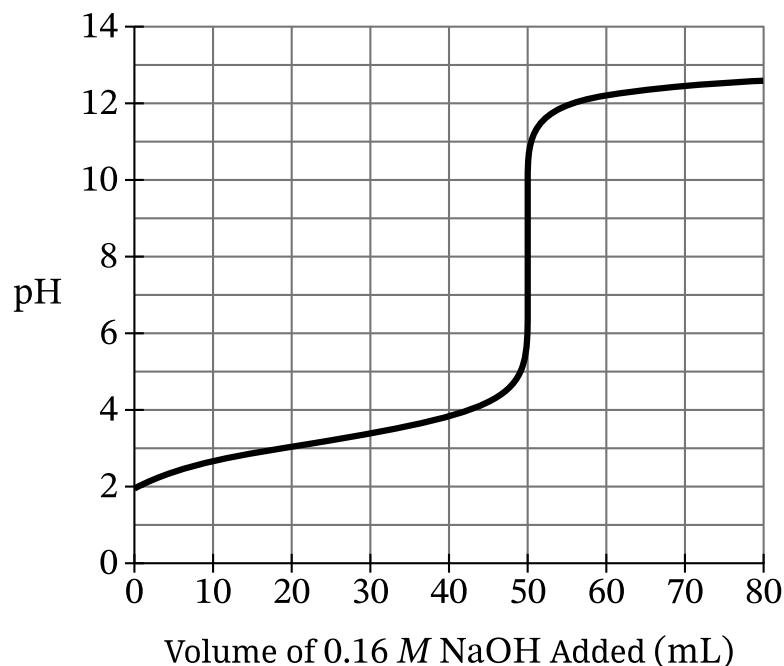
The following information applies to parts D, E, and F.

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.

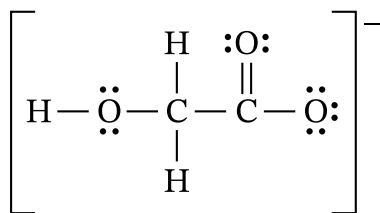
Table 2

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.

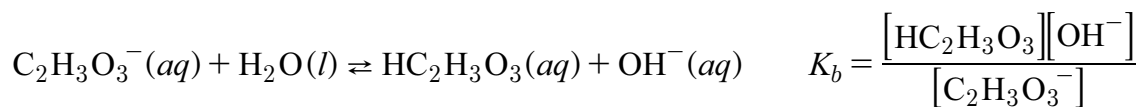
The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

7. Answer the following questions about the glycolate ion, $\text{C}_2\text{H}_3\text{O}_3^-$, 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.

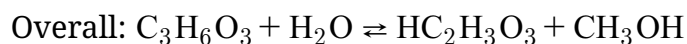
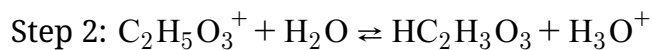
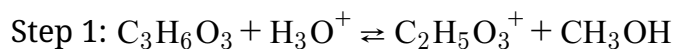
When the glycolate ion reacts with water, it forms glycolic acid, $\text{HC}_2\text{H}_3\text{O}_3$, according to the following equation. The K_b expression for the reaction is provided.



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

- Calculate the value of K_b for the glycolate ion.
- 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, $\text{C}_3\text{H}_6\text{O}_3$. A proposed mechanism for the reaction is given.



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

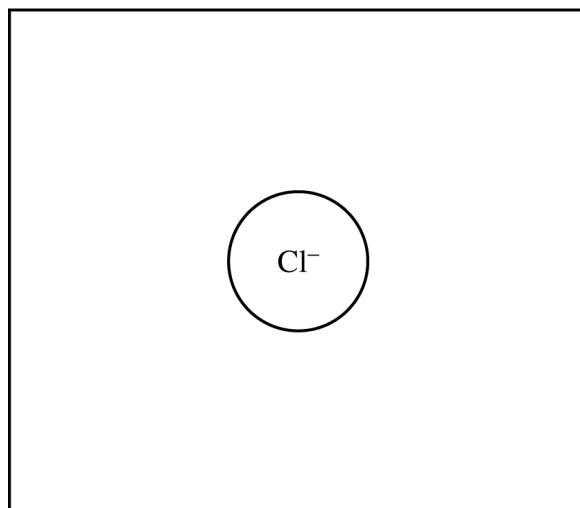
. HCl is a molecular gas as a pure substance but acts as an acid in aqueous solution.

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

(i) Calculate the number of moles of $\text{HCl}(g)$ in the container.

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

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



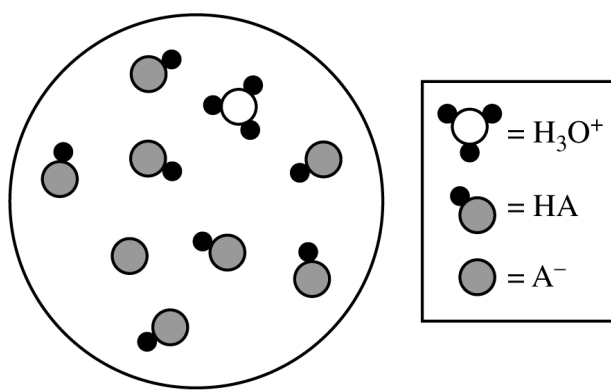
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Continue your response to **QUESTION 5** on this page.

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.

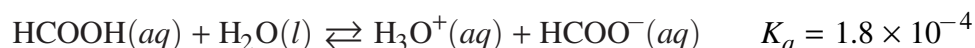
- (c) The following particulate diagram represents the ionization of one of the acids in the data table. Water molecules have been omitted for clarity. Which acid (HNO_2 , HCl , or HClO_4) is represented in the diagram? Justify your answer using the information in the table.

**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.

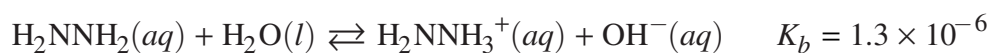
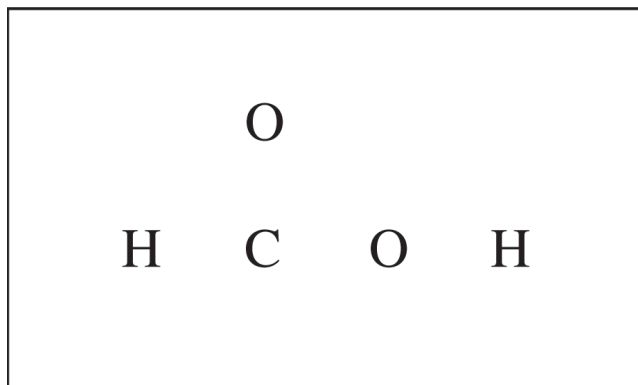
(a) Write the expression for the equilibrium constant, K_a , for the reaction.

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

GO ON TO THE NEXT PAGE.

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 $\text{HCOOH}(aq)$.

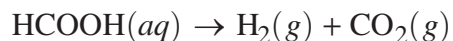
(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH .

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

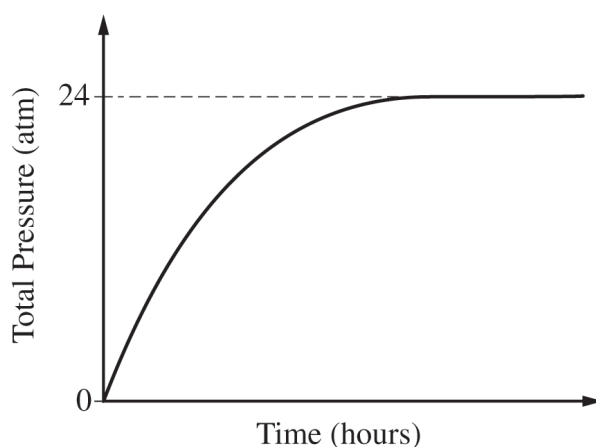
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When a catalyst is added to a solution of $\text{HCOOH}(aq)$, the reaction represented by the following equation occurs.



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



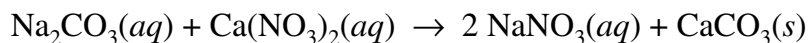
(f) The reaction occurs in a rigid 4.3 L vessel at 25°C , and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $\text{CO}_2(g)$ produced in the reaction. (Assume that the amount of $\text{CO}_2(g)$ dissolved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

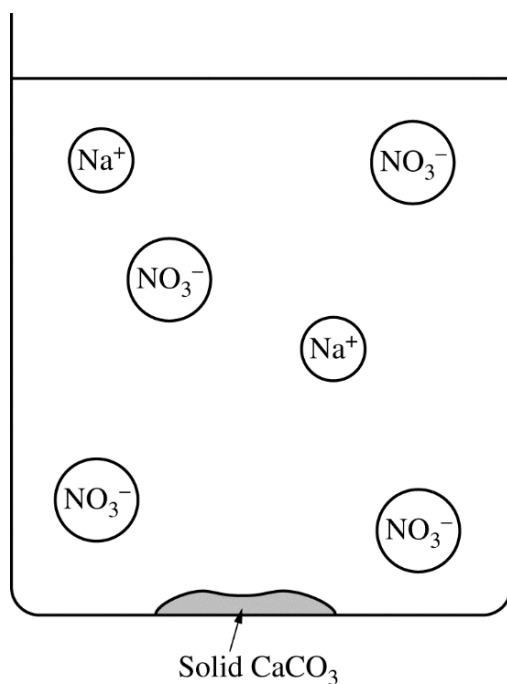
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3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $\text{Ca}(\text{NO}_3)_2(aq)$, causing a precipitate to form. The balanced 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.

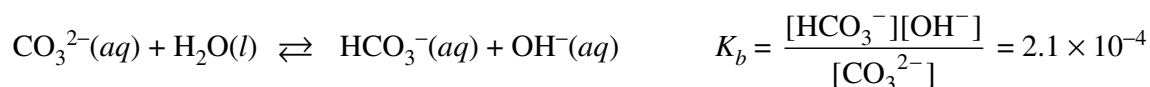


The student filters and dries the precipitate of CaCO_3 (molar mass 100.1 g/mol) and records the data in the table below.

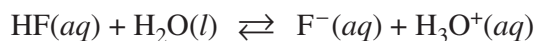
Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $\text{Ca}(\text{NO}_3)_2$ added	100.0 mL
Mass of CaCO_3 precipitate collected	0.93 g

- (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.



5. The ionization of $\text{HF}(aq)$ in water is represented by the equation above. In a 0.0350 M $\text{HF}(aq)$ 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 $\text{HF}(aq)$ 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.)

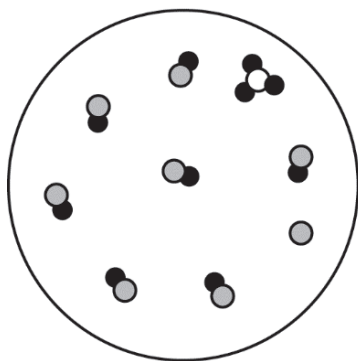
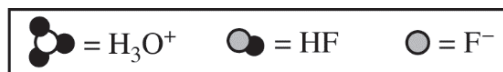


Figure 1

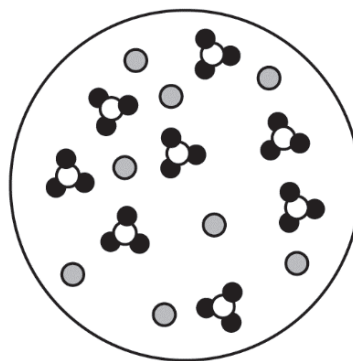
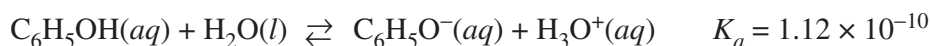


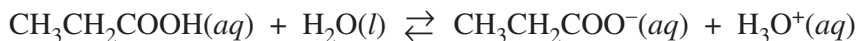
Figure 2

- (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 $\text{HF}(aq)$, will the percent ionization of $\text{HF}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.



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 $\text{C}_6\text{H}_5\text{OH}(aq)$ solution?
- (b) For a certain reaction involving $\text{C}_6\text{H}_5\text{OH}(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $\text{C}_6\text{H}_5\text{O}^-(aq)$. In order to ensure that the $\text{C}_6\text{H}_5\text{OH}(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle each pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($\text{C}_6\text{H}_5\text{O}^-(aq)$). Justify your answer.

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



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.