Introduction

Acids vary greatly in their strength—their ability to ionize or produce ions when dissolved in water. What factors determine the strength of an acid? In this experiment, the strength of acids will be measured by determining the equilibrium constants for their ionization reactions in water.

Background

The modern Brønsted definition of an acid relies on the ability of the compound to donate hydrogen ions to other substances. When an acid dissolves in water, it donates hydrogen ions to water molecules to form $\text{H}_3\text{O}^+$ ions. The general form of this reaction, called an ionization reaction, is shown in Equation 1, where $\text{HA}$ is the acid and $\text{A}^-$ its conjugate base after loss of a hydrogen ion. The double arrows represent a reversible reaction.

$$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{A}^-(aq) + \text{H}_3\text{O}^+(aq) \quad \text{Equation 1}$$

The equilibrium constant expression ($K_a$) for the reversible ionization of an acid is given in Equation 2. The square brackets refer to the molar concentrations of the reactants and products.

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \quad \text{Equation 2}$$

Not all acids, of course, are created equal. The strength of an acid depends on the value of its equilibrium constant $K_a$ for Equation 1. Strong acids ionize completely in aqueous solution. The value of $K_a$ for a strong acid is extremely large and Equation 1 essentially goes to completion—only $\text{H}_3\text{O}^+$ and $\text{A}^-$ are present in solution. Weak acids, in contrast, ionize only partially in aqueous solution. The value of $K_a$ for a weak acid is much less than one and Equation 1 is reversible—all species ($\text{HA}$, $\text{A}^-$, and $\text{H}_3\text{O}^+$) are present at equilibrium.

Polyprotic acids contain more than one ionizable hydrogen. Ionization of a polyprotic acid occurs in a stepwise manner, where each step is characterized by its own equilibrium constant ($K_{a1}$, $K_{a2}$, etc.). The second reaction (removal of the second acidic hydrogen) always occurs to a much smaller extent than the first reaction, and so $K_{a2}$ is always significantly smaller than $K_{a1}$. Sulfuric acid ($\text{H}_2\text{SO}_4$) and phosphoric acid ($\text{H}_3\text{PO}_4$) are examples of polyprotic acids.

$$\text{H}_2\text{A(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HA}^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}]} \quad \text{Equation 3}$$

$$\text{HA}^-(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{A}^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = \frac{[\text{A}^{2-}][\text{H}_3\text{O}^+]}{[\text{HA}^-]} \quad \text{Equation 4}$$

The ionization constant of a weak acid can be determined experimentally by measuring the $\text{H}_3\text{O}^+$ concentration in a dilute aqueous solution of the weak acid. This procedure is most accurate when the solution contains equal molar amounts of the weak acid and its conjugate base. Consider acetic acid as an example. Acetic acid ($\text{CH}_3\text{COOH}$) and the acetate anion ($\text{CH}_3\text{COO}^-$) represent a conjugate acid–base pair. The equilibrium constant expression for ionization of acetic acid is shown in Equation 5. If the concentrations of acetic acid and acetate ion are equal, then these two terms cancel out in the equilibrium constant expression, and Equation 5 reduces to Equation 6.
In this experiment, solutions are prepared in which the molar concentrations of an unknown acid and its conjugate base are equal. The pH of these solutions are then equal to the pKₐ for the acid. The definition of pKₐ is closely related to that of pH. Thus, pH = −log[H₃O⁺] and pKₐ = −logKₐ. The substances tested are salts of polyprotic acids that still contain an ionizable hydrogen. Sodium bisulfate (NaHSO₄), for example, is a weak acid salt; it contains Na⁺ and HSO₄⁻ ions. The HSO₄⁻ ion is a weak acid—the equilibrium constant for ionization of HSO₄⁻ corresponds to Kₐ₂ for sulfuric acid.

\[
\text{NaHSO}_4 + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) \quad \text{Equation 7}
\]

\[
\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \quad \text{Equation 8}
\]

**Experiment Overview**

The purpose of this experiment is to measure the pKₐ value for ionization of two unknown weak acids. Solutions containing equal molar amounts of the weak acids and their conjugate bases are prepared by “half-neutralization” of the acid. Their pH values are measured and used to calculate the pKₐ value for the unknowns and thus determine their identities.

**Pre-Lab Questions**

Phosphoric acid is a triprotic acid (three ionizable hydrogens). The values of its stepwise ionization constants are \( K_{a1} = 7.5 \times 10^{-3} \), \( K_{a2} = 6.2 \times 10^{-8} \), and \( K_{a3} = 4.2 \times 10^{-13} \).

1. Write the chemical equation for the first ionization reaction of phosphoric acid with water.

2. Write the equilibrium constant expression (\( K_{a1} \)) for this reaction.

3. What would be the pH of a solution when \([\text{H}_3\text{PO}_4]\) = \([\text{H}_2\text{PO}_4^-]\)? \( \text{Note: pH} = -\log[\text{H}_3\text{O}^+] \).

4. Phenolphthalein would not be an appropriate indicator to use to determine \( K_{a1} \) for phosphoric acid. Why not? Choose a suitable indicator from the following color chart.

| Indicator    | pH  
|--------------|------
|              | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10   | 11   |
| Phenolphthalein | Colorless | Pink | Red |
| Methyl Red    | Red   | Orange | Yellow |
| Orange IV     | Orange | Peach | Yellow |
Materials:

- Unknown weak acids, A–E, about 0.5 g each
- Phenolphthalein solution, 0.5%, 1 mL
- Sodium hydroxide solution, NaOH, 0.1 M, 15 mL
- Wash bottle and distilled or deionized water
- pH Meter
- Weighing dishes, 2
- Balance, centigram (0.01-g precision)
- Beaker, 150-mL
- Erlenmeyer flask, 125-mL
- Graduated cylinder, 50- or 100-mL
- Pipets, Beral-type, 2
- Stirring rod

Safety Precautions Acids and bases are skin and eye irritants. Avoid contact of all chemicals with eyes and skin. Inform the teacher and clean up all acid and base spills immediately. Phenolphthalein is an alcohol-based solution and is flammable. Keep the solution away from flames. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory.

<table>
<thead>
<tr>
<th>pH</th>
<th>A</th>
<th>Sample #1</th>
<th>Sample #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Sample #1</td>
<td>Sample #2</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Sample #1</td>
<td>Sample #2</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Sample #1</td>
<td>Sample #2</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Sample #1</td>
<td>Sample #2</td>
<td></td>
</tr>
</tbody>
</table>

Procedure

1. Label two weighing dishes #1 and #2.
2. Obtain an unknown weak acid and record the unknown letter in the Data Table.
3. Measure out a small quantity (0.15–0.20 g) of the unknown into each weighing dish. Note: It is not necessary to know the exact mass of each sample.
4. Using a graduated cylinder, precisely measure 50.0 mL of distilled water into a 150-mL beaker.
5. Transfer sample #1 to the water in the beaker and stir to dissolve.
6. Using a graduated cylinder, precisely transfer 25.0 mL of the acid solution prepared in step 5 into an Erlenmeyer flask.
7. Add 3 drops of phenolphthalein solution to the acid solution in the Erlenmeyer flask.
8. Using a Beral-type pipet, add sodium hydroxide solution dropwise to the flask. Gently swirl the flask while adding the sodium hydroxide solution.
9. Continue adding sodium hydroxide dropwise and swirling the solution until a faint pink color persists throughout the solution for at least 5 seconds. This is called the endpoint. Note: A pink color develops immediately when the base is added, but fades quickly once the solution is swirled. When nearing the endpoint, the pink color begins to fade more slowly. Proceed cautiously when nearing the endpoint, so as not to “overshoot” it.

Note: At this point the solution in the beaker contains exactly one-half of the original amount of acid, essentially all of which
is in the acid form, HA. The Erlenmeyer flask contains an equal amount of the conjugate base, A\textsuperscript{-}, obtained by neutralization.

1. Pour the contents of the Erlenmeyer flask back into the beaker. Pour the solution back and forth a few times to mix. \textit{Note:} It is important to transfer the solution as completely as possible from the flask back into the beaker.

2. Using a pH meter, measure the pH of the resulting solution in the beaker, which contains equal molar amounts of the acid and its conjugate base. Record the pH in the Data Table.

3. Dispose of the beaker contents according to the teacher’s instructions and rinse both the beaker and the Erlenmeyer flask with distilled water. Dry the beaker with a paper towel.

4. Repeat steps 4–12 using sample #2.

5. Repeat steps 1–13 for one of the remaining unknowns.

\textbf{Calculations / Data Analysis}

1. Average the pH readings for each trial (samples #1 and #2) to calculate the average pK\textsubscript{a} value for the unknown weak acids and enter answers in a Results Table.

2. The following table lists the identities of the unknowns in this experiment. Calculate the pK\textsubscript{a} value for each acid. \textit{Note:} pK\textsubscript{a} = −logK\textsubscript{a}. Record in a Results table.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>(K_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium dihydrogen phosphate</td>
<td>KH\textsubscript{2}PO\textsubscript{4}</td>
<td>(K_{a2}) of H\textsubscript{3}PO\textsubscript{4} = 6.2 \times 10^{-8}</td>
</tr>
<tr>
<td>Potassium hydrogen sulfate</td>
<td>KHSO\textsubscript{4}</td>
<td>(K_{a2}) of H\textsubscript{2}SO\textsubscript{4} = 1.0 \times 10^{-2}</td>
</tr>
<tr>
<td>Potassium hydrogen phthalate</td>
<td>KHC\textsubscript{6}H\textsubscript{4}O\textsubscript{4}</td>
<td>(K_{a2}) of H\textsubscript{2}C\textsubscript{6}H\textsubscript{4}O\textsubscript{4} = 3.9 \times 10^{-4}</td>
</tr>
<tr>
<td>Potassium hydrogen tartrate</td>
<td>KHC\textsubscript{6}H\textsubscript{6}O\textsubscript{6}</td>
<td>(K_{a2}) of H\textsubscript{2}C\textsubscript{4}H\textsubscript{6}O\textsubscript{6} = 4.6 \times 10^{-5}</td>
</tr>
<tr>
<td>Acetylsalicylic acid</td>
<td>2-CH\textsubscript{3}CO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}COOH</td>
<td>(K_a = 3.2 \times 10^{-4})</td>
</tr>
</tbody>
</table>

3. Compare the experimental pK\textsubscript{a} value for each unknown with the calculated values reported in Question 3. Determine the probable identity of each unknown and enter the answers in the Results Table.

4. Write separate equations for each unknown potassium salt dissolving in water and for the ionization reaction of the weak acid anion that each of these salts contains. (See Equations 7 and 8.)

5. Calculate percent error for each unknown.

\textbf{Error Analysis (Discussion)}

- Comment on the precision (reproducibility) of the experimental pK\textsubscript{a} determinations.
- Describe three sources of experimental error and its likely effect on the pK\textsubscript{a} values.

\textbf{Conclusion/Questions}

- Explain the concept; i.e. why can a weak acid’s pK\textsubscript{a} be calculated?
- Why was it not necessary to know the exact mass of each acid sample?
- Why was it not necessary to know the exact concentration of the sodium hydroxide solution?
- Why was it necessary to measure the exact volume of distilled water used to dissolve the acid, as well as the exact volume of solution transferred from the beaker to the Erlenmeyer flask?