**K_a for Unknown Acid**

**METHOD OF PARTIAL NEUTRALIZATION**

**DISCUSSION:**

Look at the ionization equilibrium of a weak acid:

\[ HA (aq) + H_2O \rightleftharpoons H_3O^+ (aq) + A^- (aq) \]

\[ K_a = \frac{[H^+] [A^-]}{[HA]} \]

This may also be written as:

\[ K_a = [H^+] \cdot \frac{[A^-]}{[HA]} \quad (1) \]

You do not need to know both \([A^-]\) and \([HA]\), only their ratio to calculate \(K_a\) from the observed pH.

When you begin to titrate an acid, you start to convert that acid to salt:

\[ HA + NaOH \rightarrow H_2O + NaA \]

acid \hspace{0.5cm} salt

If you stop before you reach the end point, you will have excess **ACID** still un-neutralized in the beaker along with the **SALT** that has been formed. At this point the acid is very little ionized because of the effect of the salt present. So you can consider the acid to be almost entirely in the form of HA molecules. The \(A^-\) ion comes almost entirely from the salt, for the same reason, effect of excess \(A^-\) on the acid’s ionization. So the ratio we want in equation (1) above, \([A^-]/[HA]\), is simply the salt-to-acid ratio.

To know the salt to acid ratio, you need only to know how far toward the endpoint you have gone. For example, at one-fifth the way to the end point you have neutralized (formed salt from) one-fifth of your acid. The other four-fifth is still un-neutralized. So your mixture is 1/5 salt and 4/5 acid. The salt to acid ratio is 1/5 to 4/5.

\[ HA + NaOH \rightarrow H_2O + NaA \]

\[ \text{acid}=4/5 \hspace{0.5cm} \text{salt}=1/5 \]

In terms of net-ionic equation the above equation could be written as:

\[ HA + OH^- \rightarrow H_2O + A^- \]

\[ \text{acid} \hspace{0.5cm} \text{conjugate base} \]

Since \[ \frac{\text{salt}}{\text{acid}} = \frac{1/5}{4/5} \], then \[ \frac{[A^-]}{[HA]} = \frac{1/5}{4/5} \]
Substituting into (1) above, we find:

\[ K_a = [H^+] \cdot \left(\frac{1/5}{4/5}\right) \]

In today’s experiment you will first determine \( K_a \) of an unknown acid by measuring the pH of the pure acid (no salt present). Next you will titrate the acid to find what volume of base is needed to neutralize it completely.

Then you will make several known mixtures, in which the acid is 1/4 neutralized, 1/2 neutralized, and 3/4 neutralized. From the salt-to-acid ratio and the measured pH for each solution, you will calculate \( K_a \).

Averaging the four \( K_a \) values calculated (for the pure acid solution and for the three mixtures of salt-plus-acid) should give a more reliable value than you would obtain from a single determination.

**PRECISION OF \( K_a \) MEASUREMENTS**

pH cannot be determined with the same precision as titration measurements. But high precision is not necessary for equilibrium constants. Here it is the order of magnitude that is of primary interest, that is, the value of the exponent. The numerical part is usually recorded to only one or two significant figures, and may even be left off entirely.

For example, \( K_a \) for \( HC_2H_3O_2 \) = \( 1.8 \times 10^{-5} \sim 10^{-5} \)
LABORATORY TECHNIQUES:

A pipet is a tube designed to deliver a specific known volume of solution with a high degree of accuracy. You will use a 10.00 ml pipet which has only one calibration mark. You will use a pipet pump to draw liquid into the pipet.

PIPET OPERATING INSTRUCTIONS:

The pipet that you will check out from the stockroom is clean and dry. Do not rinse it with water.

Your instructor will demonstrate the operating procedure which may be summarized as:

1. Hold the pipet close to the upper end and insert the chuck of the pump with a slight pressure and twist. This assures a secure fit. WARNING: EXTREME CARE SHOULD BE TAKEN WHEN INSERTING THE PIPIET BECAUSE OF THE POSSIBILITY OF SHATTERING. To loosen the pipet, hold it near the chuck, twist slightly and pull.

2. Submerge the end of the pipet into the solution and turn the operating wheel with the thumb. Fluid will be drawn up into the pipet. To expel fluid, turn the wheel in the opposite direction. For fast emptying, press down on the plunger top. Some liquid will remain in the tip. It is meant to stay there. Never blow out the last liquid from the pipet; if you do, you will get more than the intended volume of the sample.

3. To rinse the pipet between solutions, draw in a little of the next sample to be used. Rotate the pipet so that the liquid covers all surfaces below the calibration mark, then throw the rinse liquid away.

EXPERIMENT:

1. Use a slip to sign out a buret, a 10.00 ml pipet, a pipet pump, and a pH pen.

2. Take your lab report and a clean dry 125 ml Erlenmeyer flask to your instructor who will put an unknown acid solution in your flask.

3. Determine the pH of your unknown acid, using the pH pen. From your observed pH calculate \([H^+]\).

4. Pipet 10.00 ml of unknown acid into a 125 ml Erlenmeyer flask and titrate with the standard base provided, using phenolphthalein indicator. (Use a minimum volume of standard base. Probably you will need less than 40 ml total for all parts of the experiment.) The NaOH solution will be approximately 0.1 M but be sure to record its exact molarity given on the bottle.
5. Calculate the molarity of your unknown acid solution, which will be a monoprotic acid.

6. Calculate the value of $K_a$ from the molarity and from the value of $[H^+]$ obtained above.

7. a. Pipet another 10.00 ml of unknown acid into a clean 125 ml Erlenmeyer flask. Add from the buret exactly one-fourth of the volume needed above for complete neutralization. Mix well, then transfer the mixture to 50 ml beaker, measure and record the pH.

   b. Repeat using 10.00 ml of unknown plus one-half the volume NaOH needed to neutralize it completely. Measure the pH of this mixture after transferring it to a 50 ml beaker.

   c. Repeat again with the acid three-fourth neutralized. Measure pH.

8. Average all four values of $K_a$ of your unknown acid. Then ask your instructor for the accepted value of your acid. Report the precision and the accuracy of our $K_a$ determination.
Report Sheet

Kₐ FOR UNKNOWN ACID
BY PARTIAL NEUTRALIZATION METHOD

Name__________________________  Last    First
Instructor’s Initial________

1. pH of unknown acid
pH= ____________

2. Calculate the [H⁺] from measured pH
[H⁺]= ____________M

3. Volume of unknown acid used
Acid used= 10.00 ml

4. Titration:

<table>
<thead>
<tr>
<th>initial buret reading</th>
<th>final buret reading</th>
<th>Volume of NaOH setup:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>= ____________ml</td>
</tr>
</tbody>
</table>

5. Molarity of NaOH (written on the bottle)
M_{NaOH}= ____________M

6. Consider the equation for the titration reaction to calculate the molarity of the unknown acid:

\[
\text{HA (aq) + OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^- \quad \text{acid} \quad \text{conjugate base}
\]

Setup:

Molarity of unknown acid ____________ M

7. Kₐ of unknown acid:
Equilibrium equation

\[
\text{HA (aq) + H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq)
\]

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>_____</th>
<th>_____</th>
<th>_____</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in concentration</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
</tbody>
</table>
Equilibrium expression:

\[ K_a = [H^+] \cdot \frac{[A^-]}{[HA]} \]

Calculate \( K_a \) of unknown acid:

**Setup:**

\[ K_a = \ldots \]

8. **Partial Neutralization Mixtures:**

<table>
<thead>
<tr>
<th>Initial buret reading</th>
<th>Final buret reading</th>
<th>ml base</th>
<th>([A^-]/[HA])</th>
<th>(pH_{measured})</th>
<th>([H^+]_{calculated})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td></td>
<td></td>
<td>([1/4] [3/4])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b.</td>
<td></td>
<td></td>
<td>([1/2] [1/2])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c.</td>
<td></td>
<td></td>
<td>([3/4] [1/4])</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculation of \( K_a \) by partial neutralization mixtures.

a. **Setup:**

\[ K_a = \ldots \]

b. **Setup:**

\[ K_a = \ldots \]

c. **Setup:**

\[ K_a = \ldots \]
9. Average of four experimental values for $K_a$:
   Setup:

   Average $K_a = \underline{\hspace{2cm}}$

10. Precision: (standard deviation)
    Setup:

11. Accepted value of $K_a$ for unknown (from instructor):
    $K_a = \underline{\hspace{2cm}}$

12. Accuracy of $K_a$ determined:
    Setup:

    $\pm \underline{\hspace{2cm}}$

    $\underline{\hspace{2cm}} \%$
Exercise:
1. 44.70 ml of 0.100 M NaOH are required to completely neutralize 50.00 ml of a weak monoprotic acid, HA. When 34.43 ml of NaOH are added to another 50.00 ml of the acid, the pH reading was 4.80. Calculate $K_a$ for the acid using the partial neutralization method.

Setup:
2. The pH of a weak monoprotic acid, HA, is 4.55. It took 39.22 ml of 0.2334 M NaOH to titrate 25.00 ml of the acid.

a. Write an equation for the above reaction.

b. Calculate the molarity of the weak acid.
Setup:

\[ [\text{HA}] \] M

c. Write the equilibrium equation. Construct a table showing initial conc., change in conc., and equilibrium conc. Calculate the ionization constant, \( K_a \), for the above acid.
Setup:

Answer ________

d. 23.55 ml of the NaOH were added to partially neutralize a new 25.00 ml sample of the acid. The pH of the mixture was measured as 5.33. Calculate \( K_a \) for the acid, HA, using the partial neutralization method.
Setup:

Answer ________