EXPERIMENT 9B
STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

PURPOSE:

To standardize a solution of sodium hydroxide by titration with a primary standard, ($KHC_8H_4O_4$), potassium hydrogen phthalate ($KHC_8H_4O_4$)

PRINCIPLES:

Most shelf reagents, such as 0.10 M sodium hydroxide, could not be kept at a previously determined accurate concentration, because the concentration of these reagents changes in time, due to exposure to the environment.

In order to obtain a reagent of accurately known concentration, expressed to four significant figures, the concentration of the reagent must be determined by reacting it with a known amount of another reagent. The entire procedure by which the molarity of a solution of one substance (NaOH) is obtained from an accurately known amount of another substance, commonly referred to as a primary standard, is called standardization**.** The preferred method commonly used for the standardization of NaOH is an Acid – Base titration with **potassium hydrogen phthalate** ($KHC_8H_4O_4$, thereafter abbreviated as KHP) used as a primary standard.

Potassium hydrogen phthalate (KHP) is a soluble salt, and is completely dissociated in aqueous solution.

$$KHP(aq) \longrightarrow K^+(aq) + HP^-(aq)$$

Hydrogen phthalate ion

The hydrogen phthalate ion, HP^- is a weak acid and it undergoes partial ionization:

$$HP^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + P^{2-}(aq)$$

The addition of NaOH to this equilibrium system will cause the OH^- ions to combine with the hydronium (H_3O^+) ions to form water.

$$OH^-(aq) + H_3O^+(aq) \longrightarrow H_2O(l)$$

The decrease in the concentration of hydronium (H_3O^+) ions will cause the equilibrium system to shift to the right and, as a result, more of the weak acid (hydrogen phthalate ion, HP^-) will ionize. Successive additions of NaOH will continually remove H_3O^+ ions, shift the ionization equilibrium of the weak acid (hydrogen phthalate ion, HP^-) to the right and force the weak acid into complete ionization.

The situation can be summarized in the equilibrium table below:

Equation:	$HP^-(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$P^{2-}(aq)$
Stress:			decreases	
Shift:		→		
New Equilibrium:	**decreased**	**decreased**	**decreased**	**increased**

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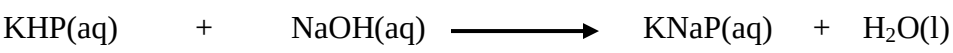
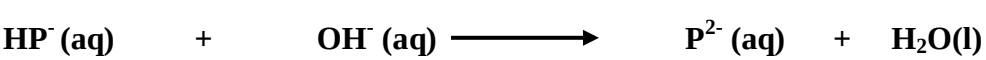
The net result is the complete neutralization of potassium hydrogen phthalate (KHP) by the NaOH solution, as shown in the equations below:



Net Ionic Equation:



Note that according to the stoichiometry of the reactions involved here:
Number of moles of KHP = Number of moles of HP^- = Number of moles of NaOH
Or simply:

Number of moles of KHP = Number of moles of NaOH

If an accurately determined mass of KHP is used for the titration the number of moles of KHP is known and, as such, the number of moles of NaOH used to completely neutralize the weak acid is also known. The challenge is to experimentally determine by titration the exact volume of NaOH required to completely neutralize the known mass of the weak acid (potassium hydrogen phthalate, KHP).
This is achieved by slowly adding the NaOH solution of unknown concentration to the solution containing an accurately determined mass of KHP, while the pH is monitored with either a **pH meter (Method I)** or an **indicator (Method II)**.

As the acid and the base combine, they neutralize each other. At the **equivalence point** – the point in the titration when the number of moles of base is equal to the number of moles of acid – the titration is complete.
Two common methods are available to experimentally determine the exact volume of NaOH required to reach the equivalence point of this acid – base titration.

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Method I: Determining the Equivalence Point by a "pH Titration"

This method concentrates on the pH changes that occur during the titration
A plot of the pH of the solution during a titration (shown below) is known as a **titration curve** or a **pH curve**

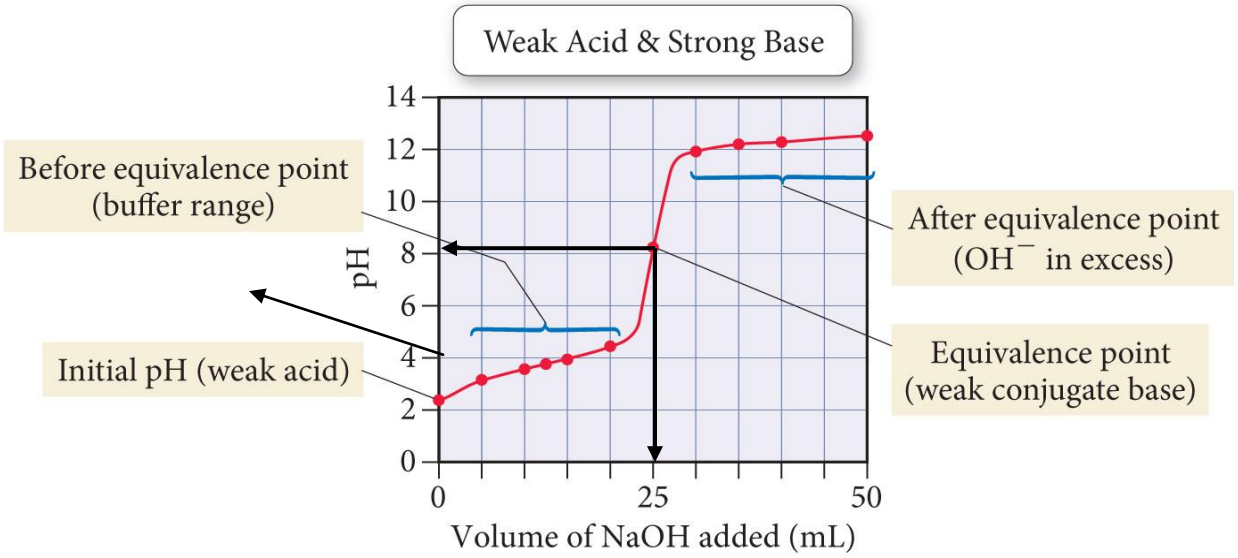

Figure 1

Before any base (NaOH) is added to the solution, the pH is low (as expected for a solution of a weak acid). As small amounts of NaOH are added, the added NaOH converts the stoichiometric amount of the weak acid (Hydrogen phthalate ion, HP^-) into its conjugate base (phthalate ion, P^{2-}). The solution now contains significant amounts of both a weak acid (hydrogen phthalate ion, HP^-) and its conjugate base (phthalate ion, P^{2-}). The solution is now a buffer.
As more NaOH is added, the NaOH converts more of the weak acid (Hydrogen phthalate ion, HP^-) into its conjugate base (phthalate ion, P^{2-}).The point of inflection in the middle of the curve is the equivalence point. Notice that the pH changes very quickly near the equivalence point (small amounts of added base cause large changes in pH).
At the equivalence point all of the weak acid (hydrogen phthalate ion, HP^-) has been converted into its conjugate base (phthalate ion, P^{2-}) and the solution is no longer a buffer, since it no longer contains significant amounts of both a weak acid and its conjugate base. Instead, the solution contains only a weak base (phthalate ion, P^{2-}).
As a result, the pH at <u>the equivalence point</u> is NOT neutral, but basic.
The titration of a weak acid by a strong base always has a basic equivalence point because at the equivalence point all of the weak acid has been converted into its conjugate base, resulting in a weakly basic solution.
Beyond the equivalence point, the solution is basic because the weak acid (Hydrogen phthalate ion, HP^-) has been completely neutralized and excess base is added to the solution.

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While the procedure for determining the equivalence point from a titration curve (pH measurements during the titration) is much slower than the one employing an indicator, this method has more versatile uses than the standardization using an indicator.
A "pH Titration", also referred to as a "Titration Curve" can be used to:

1. **Standardize a solution of 0.10 M sodium hydroxide (NaOH) solution,**
2. **Determine the Acid Ionization Constant of a Weak Acid by the half – equivalence point method.**
3. **Allow a chemist to choose an appropriate indicator for subsequent titrations of similar samples with the same reagent, as illustrated below.**

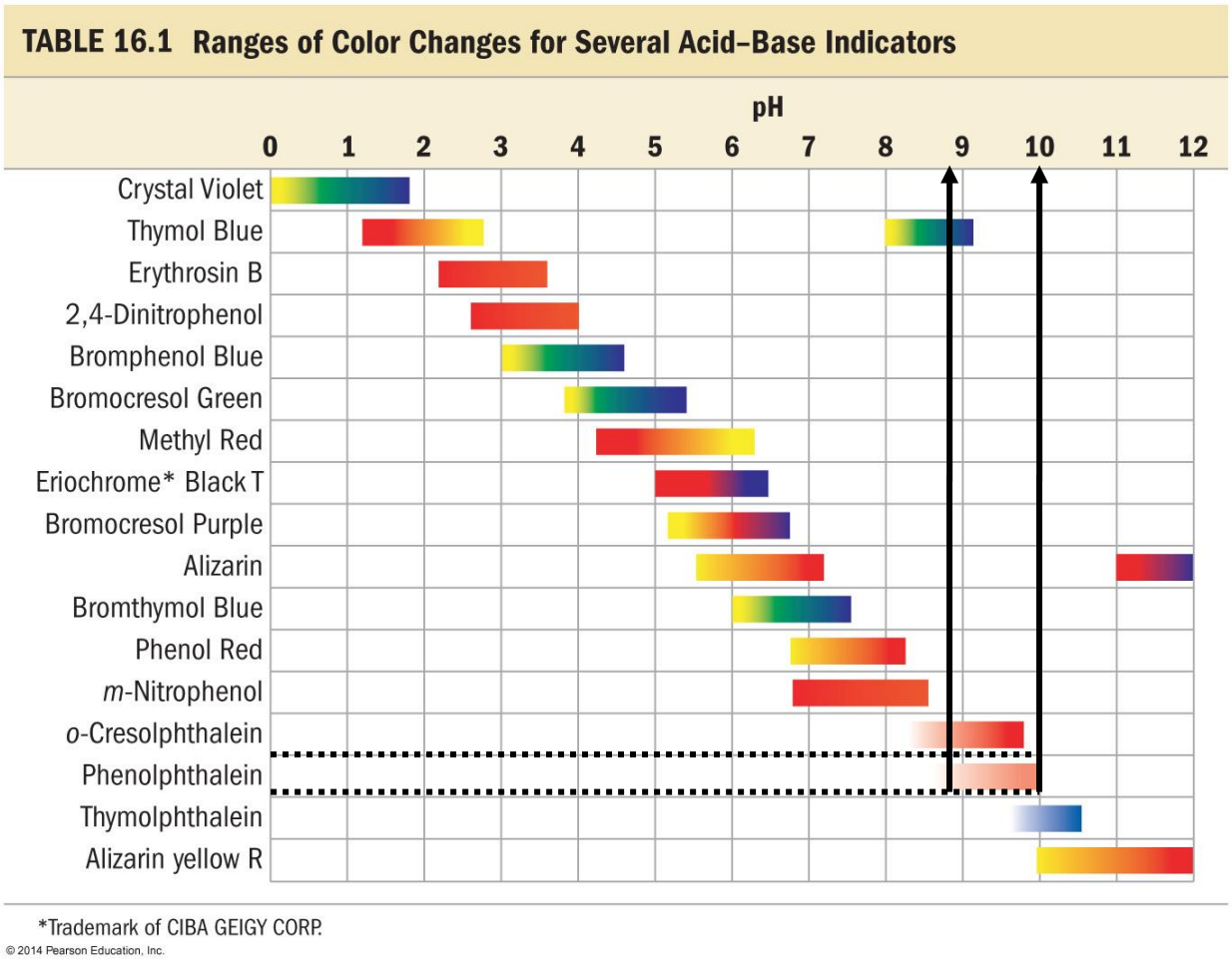

Figure 2

The figure above shows that phenolphthalein (color change between pH = 8.7 – 10) would be the correct indicator for the titration of a weak acid with a strong base since, as previously explained, the equivalence point for such a titration occurs in the range of a basic pH.

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Method II: Determining the Equivalence Point by the use of an "Indicator"

The exact volume of NaOH required to reach the equivalence point is determined by the use of an indicator. With an indicator, we rely on the point where the indicator changes color – called the **end point** – to determine the equivalence point (when the amount of acid equals the amount of base). With the correctly chosen indicator, the end point of a titration (indicated by the color change) occurs at the equivalence point.

After the indicator is added to the solution containing the primary standard, the NaOH solution of unknown concentration is delivered carefully from a buret, until the indicator changes color. The indicator chosen will have one color before the reaction is complete (before the equivalence point is reached) and another color when the completion occurs (the equivalence point is reached). The color change of the solution signals the exact completion of the reaction.

This is the method that will be used in this experiment.

As mentioned above, in this experiment we use an indicator and we rely on the point where the indicator changes color – called the "**End Point**" – to determine the "**Equivalence Point**".

- **End Point**
  The point in the titration where the indicator changes color.

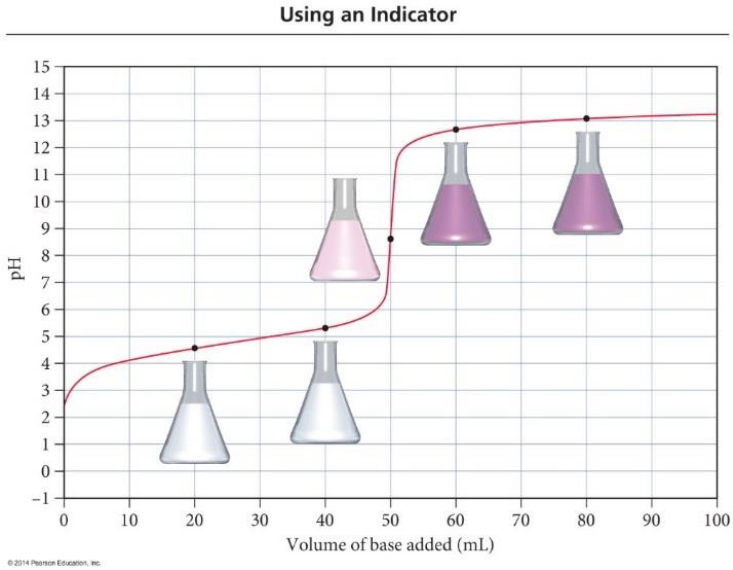

Figure 3

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- **Equivalence Point**

The point in the titration when the number of moles of acid used equals exactly the number of moles of base added.

Ideally, the indicator chosen will have one color before the reaction is complete (before the equivalence point is reached) and another color when the completion occurs (the equivalence point is reached). The color change of the solution should signal the exact completion of the reaction. However, if the indicator is not correctly chosen, the "End Point" may occur slightly before or after the "Equivalence Point", resulting in a minor experimental error. With the correctly chosen indicator, (such as **phenolphthalein**, used in this experiment) the "End Point" of the titration (indicated by the color change) occurs very closely or exactly at the "Equivalence Point".

PROCEDURE:

I. Preparation of the sodium hydroxide solution (approximately 0.1 M)

1. Measure 9.0 mL of 6 M sodium hydroxide solution in a 10 mL graduated cylinder.
2. Pour the solution into a clean 500 – mL plastic bottle. Rinse out the graduated cylinder with several portions of D.I water and add the rinses to the plastic bottle.
3. Dilute this solution to approximately 500 mL with deionized water. The volume of the sodium hydroxide solution does not have to be known accurately.
4. Stopper firmly the plastic bottle and mix the solution thoroughly by slowly inverting the plastic bottle at least ten times. Keep in mind that insufficient mixing of solutions is a common source of error in titrations.
   KEEP THE BOTTLE OF NaOH STOPPERED AT ALL TIMES!
5. Place a label on the plastic bottle indicating your name and the contents (0.1 M NaOH)
6. This solution will be titrated in the next part of the experiment against KHP, to determine its exact molarity.

II. Preparation of the KHP solution

1. Using the analytical balance, accurately weigh a sample of between **0.3g and 0.5g** of solid KHP (from a vial) into a 250 mL Erlenmeyer flask, by using the weighing bottle technique, described below.

- Remove the cap from the vial and place the vial on the analytical balance. Read and record its mass.
- Place a clean (does not have to be dry) 250 mL Erlenmeyer flask on a centigram balance, adjacent to the analytical balance.
- Do no record the mass of the empty 250 mL Erlenmeyer flask. Tare the centigram balance so that the reading on the centigram balance is 0.00 g.
- Dispense a few crystals of the KHP from the vial directly into the 250 mL Erlenmeyer flask, by taping gently the vial against the neck of the flask..
- Follow the mass readings on the centigram balance, as they increase upon the addition of the solid KHP. When the desired mass range (0.3g – 0.5g), has been reached, stop adding KHP.

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- Reweigh the vial on the analytical mass. Read and record this mass.
  The accurate mass of KHP transferred from the vial into the Erlenmeyer flask is the difference between the mass of the vial before transferring some of the solid sample into the flask (Mass of vial + KHP) and the mass of the vial after transferring the solid sample into the flask (Mass of vial – KHP).
  - **ONLY THE VIAL WILL BE PLACED ON THE ANALYTICAL BALANCE, BUT NOT THE FLASK.**
  - **THE TWO MASSES OF THE VIAL (BEFORE AND AFTER TRANSFER) MUST BE RECORDED IN FOUR SIGNIFANT FIGURES.**
  - **THERE IS NO NEED TO RECORD THE MASS READING FROM THE CENTIGRAM BALANCE.**
- Cap the vial containing the KHP and keep it capped in your locker.

2. Add to the flask, containing the KHP, about 100 mL of gently heated (about 40^0C) deionized water. You may use the 100 mL mark on the flask to estimate the volume of D.I. water added. No need to use a graduated cylinder.
If you notice that some of the solid crystals of KHP got stuck to the inner walls of the flask, wash them down into the flask with streams of D.I. water from your wash bottle.

3. Place a stirring magnet in the Erlenmeyer flask.

4. Place the flask on a stirring plate and set the stirring plate so as to provide a gentle and uniform mixing of the KHP solution. Continue mixing on the stirring plate or swirling gently until the solid acid is completely dissolved.

III. Preparation of the buret for the titration

1. Obtain a 50.0 mL buret and clean it thoroughly with deionized water.

2. Rinse the buret with three portions of about 5 mL of the sodium hydroxide solution, coating the barrel each time before emptying out the solution.

3. Fill the buret with the sodium hydroxide solution a little above the "0" line.

4. Use a buret clamp to clamp the buret

5. Open the stopcock and drain the sodium hydroxide solution in order to completely fill the tip of the buret and flush out any air bubbles caught in the tip.

6. Check the stopcock for leaks.

7. Set the level of the titrant (NaOH solution) at the 0.00 mL mark.
- Record the initial buret reading (0.00 mL preferred). It is not absolutely necessary to refill it to exactly 0.00 mL; however it is necessary to record exactly the starting volume to the nearest ± 0.01 mL.

IV. The Titrations

1. First Titration (trial run)

Before you proceed with the first titration:
- Make sure that the solid sample of KHP is completely dissolved.
- Add two drops of phenolphthalein indicator solution to the KHP solution
- Place the flask on the stirring plate and center it.
- Adjust the height of the buret so that the tip of the buret is just barely inside of the flask.

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(a) Slowly add the NaOH solution to the flask containing the KHP solution, while gently stirring the contents of the flask with the stirring magnet.
(b) As the NaOH solution is added, a pink color appears where the drops of the base come in contact with the solution. The color disappears with swirling.
(c) As the end point is approached, the color disappears more slowly, at which time the sodium hydroxide solution should be added drop by drop.
(d) The end point is reached when one drop of the sodium hydroxide solution turns the entire solution in the flask from colorless to faint pink. The solution should remain faint pink when it is swirled.
(e) Allow the titrated solution to stand for at least 1 minute, so that the buret will drain properly.
(f) Remove any hanging drop from the buret tip by touching it to the side of the flask. Then wash it down, into the flask, with a stream of D.I. water from the wash bottle.
(g) Read the final level of the NaOH solution in the buret to the nearest ± 0.01 mL (two decimals) and record it.
(h) Discard the solution and wash out the flask with plenty of tap water followed by a few rinses with D.I water

2. <u>Subsequent Titrations</u>

- Repeat the titration for a total of at least five titrations.
- By using the data from the first titration (trial run) it is possible to monitor the subsequent titrations quite efficiently and save time, by estimating the volume of NaOH needed to reach the end point.

  <u>Example</u>:
  Assume that for the first titration (trial run) **0.4032 g** of the solid acid (KHP) have been weighed out. The titration required **18.65 mL** of base (NaOH) to reach the end point. For the second titration, **0.3825 g** of the solid acid (KHP) have been weighed out. Obviously the volume of the NaOH needed to reach the end point for the second titration will be less since the mass of the solid acid weighed out is less.
  An estimate of the volume needed to reach the end point in the second titration can now easily be calculated by realizing that the volume of NaOH needed to reach the end point is directly proportional to the mass of the solid KHP weighed out.

<u>First Titration</u>	**<u>Second Titration</u>**
m = 0.4032 g	m = 0.3825 g
V = 18.65 mL	V_x = ?

$$\frac{0.4032\ \text{g}}{18.65\ \text{mL}} = \frac{0.3825\ \text{g}}{V_x} \qquad V_x = \frac{(18.65\ \text{mL})\,(0.3825\text{g})}{0.4032\ \text{g}} = \mathbf{17.69\ mL}$$

This suggests that for the second titration about 17.69 mL of NaOH are required to reach the end point. To be on the safe side, one can proceed with fast additions of NaOH until about 16.50 mL have been added. After that point, adding the NaOH drop by drop is safe and efficient and will avoid overshooting the end point.

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- **Guidelines for an accurate standardization**
  A quick check of the precision of your titrations (reproducibility of the titrations) is to calculate the ratio of g KHP/mL NaOH, at the end point, to four significant figures. This ratio should vary only in the last significant figure.
  Under ideal circumstances, the standardization process should be repeated until it is confirmed that the **g KHP/mL NaOH ratio varies only in the last significant figure**.
- A proper standardization requires a minimum of three trials that agree within plus or minus 0.5% of each other.
  - It is very unlikely that all five (or six) trials will satisfy this requirement.
  - A data evaluation process that follows this experiment will assist you in determining which trials should be kept and which trials should be rejected.
  - The procedure used for this data evaluation requires that at least half of the values obtained must be included in the calculation of the Mean Molarity. This implies that you are not allowed to discard more than two molarities if you have performed five titrations.
- **IMPORTANT NOTES**
  This experiment is performed individually. The sodium hydroxide solution and its reported Mean Molarity will be used for another experiment, involving an unknown, assigned also individually.
  The accuracy obtained in the follow up experiment will greatly depend on the accuracy of the Mean Molarity of the NaOH solution determined in this experiment. The follow up experiment is graded as an unknown on a sliding scale for 50 points. In order to earn a good grade, it is in your interest to put in the maximum effort to obtain an accurate value for the Mean Molarity for the NaOH solution.

3. Wrapping up the experiment

DO NOT DISCARD THE STANDARDIZED SOLUTION OF NaOH SINCE IT WILL BE USED IN THE NEXT EXPERIMENT.

AFTER YOU MADE SURE THAT THE BOTTLE OF NaOH SOLUTION IS TIGHTLY STOPPERED, PLACE IT IN YOUR LOCKER.

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CALCULATIONS

For ALL samples of KHP used for the titrations record and calculate:

1. The Number of Moles of KHP added.
2. The Number of Moles of NaOH that have reacted with KHP.
3. The Volume of NaOH added to react completely with the KHP.
4. The Molarity of NaOH for each of your titrations (mol/L).
   Five titrations are required, but if time allows it, six or seven titrations are highly recommended.

   NOTE:
   The Mean Molarity will be calculated after the experimental data are evaluated by the standard deviation method in the next experiment.

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REPORT FORM

NAME: _____ Date: _____

Molar Mass of Potassium Hydrogen Phthalate: 204.2 g/mol

	1st Titration	2st Titration	3st Titration	4st Titration	5st Titration	6st Titration	7st Titration
Mass of vial + KHP (g)							
Mass of vial - KHP(g)							
Mass of KHP used (g)							
Final Buret Reading (mL)							
Initial Buret Reading (mL)							
mL of NaOH used							
L of NaOH used							
Moles of KHP							
Moles of NaOH							
Volume of NaOH (L)							
Molarity of NaOH (moles/L)							

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