EXPERIMENT 11
STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

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

PRINCIPLES:
Acid-base reactions in aqueous solution represent one of the most important types of chemical reactions.

For many years **acids** were described as those substances that taste sour, turn blue litmus paper red, react with metals to produce hydrogen gas, react with carbonates and bicarbonates to produce carbon dioxide, and react with bases to form water and salt.

Similarly, **bases** were described as tasting bitter, feeling soapy or slippery to touch, turning red litmus paper blue, and reacting with acids to produce water and a salt.

In 1887, Swedish chemist Svante Arrhenius showed that some compounds containing hydrogen atoms could ionize in water to form hydrogen ions.

These substances are now known as **Arrhenius acids**.

According to Arrhenius, a solution containing excess hydrogen ions is an acid solution, and the more hydrogen ions present, the more acidic the solution.

More recent studies indicate that the hydrogen ion (H^+), or proton in aqueous solution is hydrated, producing new species called the hydronium ion, H_3O^+:

$$H^+(aq) + H_2O(l) \longrightarrow H_3O^+(aq)$$
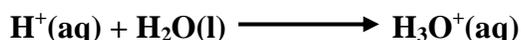
Pure water already contains small quantities of the H^+ ion (proton), H_3O^+ (hydronium ion) due to the self-ionization reaction of water, written either as:

$$H_2O(l) \rightleftharpoons H^+(aq) \;+\; OH^-(aq)$$

or

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

Acid substances may also be defined as proton (H^+) donors within the context of a given reaction, according to the description of Bronsted and Lowry (1932)

$$HCl(aq) \;+\; H_2O(l) \longrightarrow H_3O^+(aq) \;+\; Cl^-(aq)$$
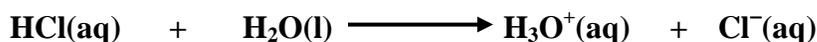
These are known as **Bronsted-Lowry acids**.
Whenever solutions of aqueous acids are discussed, the acid species in the solution is the hydronium ion.

Arrhenius bases are defined most simply as substances that generate hydroxide ions in solution:

$$NaOH(aq) \longrightarrow Na^+(aq) \;+\; OH^-(aq)$$

Bronsted and Lowry expanded the definition of a base to include any species that can accept a proton (H^+)

Such substances are now called **Bronsted-Lowry bases.**

Thus, according to Bronsted-Lowry, all hydroxides are bases, as are carbonates, bicarbonates, acetates and ammonia:

$$OH^-(aq) \quad + \quad H^+(aq) \longrightarrow H_2O(l)$$
$$CO_3^{2-}(aq) \quad + \quad H^+(aq) \longrightarrow HCO_3^-(aq)$$
$$HCO_3^-(aq) \quad + \quad H^+(aq) \longrightarrow H_2CO_3(aq)$$
$$C_2H_3O_2^-(aq) \quad + \quad H^+(aq) \longrightarrow HC_2H_3O_2(aq)$$
$$NH_3(aq) \quad + \quad H^+(aq) \longrightarrow NH_4^+(aq)$$
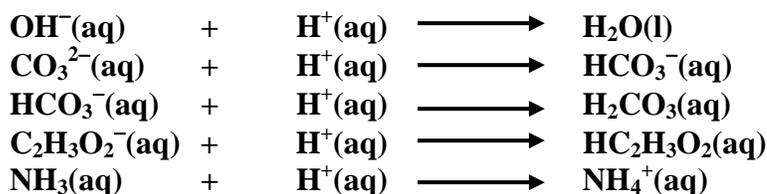
The reaction between an Arrhenius acid and an Arrhenius base, or between a Bronstead-Lowry acid-base pair is called a **neutralization reaction**.

In a complete neutralization in aqueous solution, the H_3O^+ ions react with an equal number of OH^- ions.

The neutralization of an acid releasing one H^+ ion (or H_3O^+ ion) per formula unit (monoprotic acid) with a base releasing one OH^- ion per formula unit (monohydroxy or monobasic base) exhibits a simple stoichiometry.

An example of such a reaction is illustrated by the equation describing the reaction of hydrochloric acid (a strong acid) with sodium hydroxide (a strong base):

$$HCl(aq) \quad + \quad NaOH(aq) \longrightarrow NaCl(aq) \quad + \quad H_2O$$
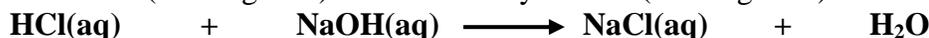
The corresponding net ionic equation for this neutralization reaction is:

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

Since $HCl(aq)$ is a strong monoprotic acid:

Number of moles of H^+ = Number of moles of acid = n_a

Since $NaOH(aq)$ is a strong monohydroxy base:

Number of moles of **OH^-** = **Number of moles of base = n_b**

Since 1 mole of H^+ uses up completely 1 mole of OH^-, it follows that the complete neutralization requires that the number of moles of acid (n_a) be equal to the number of moles of base (n_b):

$$n_a = n_b$$

This relationship can be combined with the definition of molarity:

$n_a = M_a \times V_a$ **and**   **$n_b = M_a \times V_b$**
M_a = Molarity of the acid   **M_b = Molarity of the base**
V_a = Volume of acid   **V_b = Volume of base**

It follows that: $\boxed{\mathbf{M_a \times V_a = M_b \times V_b}}$

The last relationship applies whenever the acid and base react in a 1:1 mole ratio.

STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

The stoichiometry becomes more complex when the acid and base release unequal number of H_3O^+ and OH^- ions. The neutralization of sulfuric acid with sodium hydroxide is expressed by the balanced chemical equation:

$$H_2SO_4(aq) \quad + \quad 2\,NaOH(aq) \longrightarrow Na_2SO_4(aq) \quad + \quad 2H_2O(l)$$

The 1:2 mole ratio of the acid to the base in the balanced equation indicates that twice as many moles of base are needed than of acid:

$$2n_a = n_b$$

$$2\,(M_a \times V_a) = M_b \times V_b$$

In this experiment your solution of NaOH will be standardized by titrating against a very pure sample of potassium hydrogen phthalate, $KHC_8H_4O_4$, of known mass.

Potassium hydrogen phthalate (thereafter abbreviated as KHP) is a soluble salt, and as such is completely dissociated in aqueous solution:

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

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

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

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

$$OH^-(aq) + H_3O^+(aq) \longrightarrow H_2O(l)$$
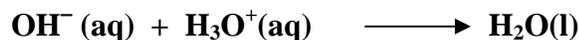
The decrease in the concentration of H_3O^+ ions will cause the equilibrium system to shift to the right and as such more of the weak acid (hydrogen phthalate ion, HP^-) will ionize. Successive additions of NaOH will continually remove H_3O^+ ions, shift the equilibrium to the right and force the weak acid into complete ionization.

This situation can be summarized in the equilibrium table below:

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

add OH^-

2 H_2O
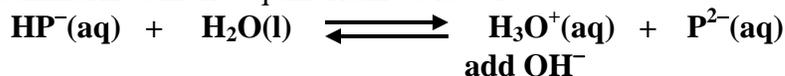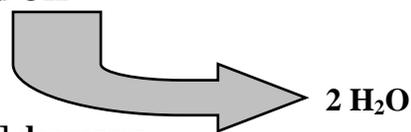
Stress: **$[H_3O^+]$ decreases**

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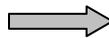
The net result is the complete neutralization of potassium hydrogen phthalate (KHP) by the NaOH solution, as shown by the equations below:

$$KHP(aq) \quad + \quad NaOH(aq) \longrightarrow KNaP \quad + \quad H_2O(l)$$

Net Ionic Equation:

$$HP^-(aq) \quad + \quad OH^-(aq) \longrightarrow P^{2-}(aq) \quad + \quad H_2O(l)$$

Number of moles of KHP = Number of moles of HP^- = Number of moles $NaOH = M_b \times V_b$

Number of moles of KHP $= M_b \times V_b$

STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

If one measures the volume (in liters) of base, V_b, required to neutralize a known mass of KHP, it is possible to calculate the molarity (M_b) of the base because the molar mass of KHP is known. The exact molarity of the NaOH solution is calculated from the mass of KHP, its molar mass, and the volume of the NaOH solution required to react completely with the KHP, as determined by a titration.

The entire procedure by which we obtain the molarity of a solution of one substance (NaOH) from an accurately known amount of another substance (KHP) is called **standardization.**

Sample Calculation:

What is the molarity of a NaOH solution if 35.75 mL of it is required to neutralize 1.0705 g of potassium hydrogen phthalate (KHP). ?

The molar mass of KHP is 204.2 g/mol

Number of moles of KHP $= 1.0705 \text{ g} \times \dfrac{1 \text{ mole KHP}}{204.2 \text{ g KHP}} = 5.24\underline{2}4 \times 10^{-3}$ moles

Number of moles of KHP = Number of moles NaOH = $5.24\underline{2}4 \times 10^{-3}$ moles

Number of moles NaOH = $\mathbf{M_b \times V_b}$

$M_b = \dfrac{5.24\underline{2}4 \times 10^{-3} \text{ moles}}{0.03575 \text{ L}} = \mathbf{0.1466 \ M}$

PROCEDURE:

1. **Preparation of approximately 0.100 M sodium hydroxide solution**
   (a) Measure 8.4 mL of 6 M sodium hydroxide solution in a 10 mL graduated cylinder.
   (b) Pour the solution into a clean 500-mL plastic bottle
   (c) Dilute this solution to approximately 500 mL with deionized water. The volume of the sodium hydroxide solution does not have to be known accurately.
   (d) Stopper firmly the plastic bottle and mix the solution thoroughly by inverting the plastic bottle at least ten times. Please note the insufficient mixing of solutions is a common source of error in titrations.
   KEEP THE BOTTLE OF NaOH SOLUTION STOPPERED AT ALL TIMES!
   (e) Place a label on the plastic bottle with indicating your name and the contents
   (**$\approx$ 0.1 M NaOH**)
   (f) This solution will be titrated in the next part of the experiment against KHP to determine its exact Molarity

2. **Standardization of the Sodium Hydroxide Solution**
   (a) Prepare about 400 – 500 mL of CO_2 – free water by boiling for about 5 minutes the deionized water.
   (b) Using the analytical balance, accurately weigh (from a vial) between 0.4g and 0.6g sample of pure potassium hydrogen phthalate into a clean 250-mL Erlenmeyer flask The flask does not have to be dry.
   Note: ONLY THE CAPPED VIAL WILL BE PLACED ON THE ANALYTICAL BALANCE, BUT NOT THE FLASK.
   Your instructor will demonstrate how to best estimate the mass of salt that must be removed from the vial.

EXPERIMENT 11
STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

(c) Add about 100 mL of CO_2 – free, deionized water to the flask, and warm gently with swirling until the salt is completely dissolved.

(d) Add two drops of phenolphthalein indicator to the solution in the flask.

(e) Rinse a previously cleaned buret with at least four 5-mL portions of the approximately 0.1 M sodium hydroxide solution that you have prepared. Discard each portion.

(f) Completely fill the buret with the sodium hydroxide solution and remove the air from the buret tip by running out some of the solution into an empty beaker.
Make sure that the lower part of the meniscus is at zero mark or slightly lower.
Remove any hanging drop from the buret tip by touching it to the side of the beaker used for washings.
Allow the buret to stand for at least 30 seconds before reading the exact position of the meniscus.
Record the initial buret reading.

(g) Slowly add the NaOH solution to your flask of KHP solution while gently swirling the contents of the flask (a magnetic stirrer if available may be used for mechanical mixing)
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.
As the end point is approached, the color disappears more slowly, at which time the sodium hydroxide solution should be added drop by drop.

(h) The end point is reached when one drop of the sodium hydroxide solution turns the entire solution in the flask from colorless to pink.
The solution should remain pink when it is swirled and after that should maintain its faint pink color for at least 30 seconds.

(i) Discard the solution and wash out the flask with plenty of tap water. Rinse with D.I. water

(j) Repeat the procedure described above with at least three more samples.

(k) From the data you obtain in at least three "good" titrations, calculate the molarity of the NaOH solution and write this molarity on the label previously placed on the bottle.

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.

EXPERIMENT 11
STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD
REPORT FORM

NAME: _____

Molar Mass of Potassium Hydrogen Phthalate: 204.2 g/mol

	1st Titration (g)	2nd Titration (g)	3rd Titration (g)	4th Titration (g)	5th Titration (g)
Initial mass of KHP + vial:					
Final mass of KHP + vial:					
Mass of KHP used:					

	1st Titration (mL)	2nd Titration (mL)	3rd Titration (mL)	4th Titration (mL)	5th Titration (mL)
Final Buret reading:					
Initial Buret reading:					
mL of NaoH used:					
L of NaOH used					

	1st Titration	2nd Titration	3rd Titration	4th Titration	5th Titration
Moles of KHP					
Moles of NaOH					
Volume of NaOH (L)					
Molarity of NaOH (moles/L)					
Average Molarity of NaOH					
Deviation* $\lvert di \rvert$					
Mean Deviation, d*					
Relative Mean* Deviation,RMD					

* See next page for explanation of terms

STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION
WITH A PRIMARY STANDARD

Deviation, $|di|$ =   is the difference between the Average Molarity and any Individual Molarity Value

   =   is expressed as an absolute value (no sign)

$$|di| = \textbf{Average Molarity – Individual Molarity Value}$$

NOTE:
If one individual deviation is much larger than the others, this is a possible indication of a "bad" titration".
You may chose not to exclude this titration from the calculation of the Average Molarity.

Mean Deviation, d   =   is the **average deviation** based on all individual deviations, $|di|$

Relative Mean Deviation   **= RMD = $\dfrac{\textbf{Mean Deviation}}{\textbf{Average Molarity}}$ x 1000 (parts per thousand)**

NOTE:
1.   The lower the RMD, the better the experimental data.
2.   Good Student Work should have an RMD of less than 5 ppt (parts per thousand)
3.   It is permitted to discard one or several "bad" titrations.
     However, for acceptable lab work, the Average Molarity should be based on at least three "good" titrations.

CONCLUSION:
For quality laboratory work, the following 2 conditions must be satisfied:

1.   The results of at least three titrations should be included in the calculation of the Average Molarity , and
2.   The three titrations and the corresponding Average Molarity should yield a calculated RMD value that is less than 5.