# Standardization of NaOH and determination of total acidity as KHP

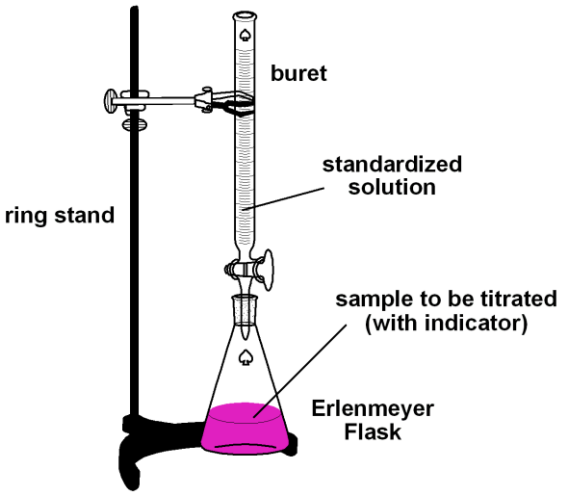
## Introduction

The purpose of this experiment is to standardize a sodium hydroxide solution and then use the standardized sodium hydroxide solution to determine the percent of KHP in an unknown sample. You will determine the total acidity in an unknown sample after standardizing solution of NaOH using the primary standard, potassium hydrogen phthalate.
A titration is an analytical procedure used to determine the concentration of a sample by reacting it with a standard solution. One type of titration uses a neutralization reaction, in which an acid and a base react to produce a salt and water.

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l) \qquad \textbf{(1)}$$

In equation 1, hydrochloric acid (HCl) and sodium hydroxide (NaOH) react to form sodium chloride (NaCl), which is also known as table salt and water. The titration proceeds until the equivalence point is reached, where the number of moles of acid is equal to the number of moles of base. This point is usually marked by observing a color change in an added indicator.

In a titration, the standard solution goes in a buret, which is a piece of glassware used to measure the volume of solvent to approximately 0.1 mL of accuracy. The solution that you are titrating goes in an Erlenmeyer flask, which should be large enough to accommodate both your sample and the standard solution you are adding.




The indicator is a weak acid (or base) itself and reacts with some of the titrant to produce the color change. An indicator changes its color as it reacts with either an acid or a base. Selecting the proper indicator is important because each indicator changes its color over a particular range of pH values. Indicators are either weak acids or weak bases. For example, phenolphthalein is a weak acid (which we will represent as HIn). In aqueous solution, the phenolphthalein dissociates slightly, forming an equilibrium.

$$HIn\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + In^-\ (aq) \qquad (2)$$

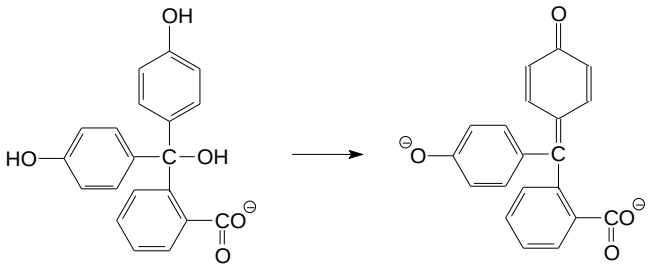
clear pink

Le Chatelier's principle states that when a system at equilibrium is subjected to an applying stress, the equilibrium will shift to relieve the stress. **In an acidic solution**, there is an excess of $H_3O^+$ ions so the equilibrium will shift to the left and favor the formation of HIn, thus we **observe a clear solution**. **In basic solution**, there is an excess of $OH^-$ ions that react with the $H_3O^+$ ions to form water. This shifts the equilibrium to the right because water is being formed and $H_3O^+$ ions are being removed, thus **we observe a pink solution**. We can use this color change to determine when the end of the titration has been achieved.

When acid is added to the indicator the **equilibrium shifts** to the left. Because the $In^{-1}$ and HIn have different colors we can see this change. When a base is added to an indicator the hydroxide ions reacts with the molecules of indicator and form indicator ions. The reaction shifts to the right.

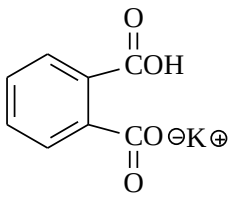
$$OH^{-1}_{(aq)} + HIn_{(aq)} \Leftrightarrow In^{-1}_{(aq)} + H_2O_{(l)}$$

Since different indicators have different $K_a$ values they change colors at different $[H^+]$, and they can be used to indicate the hydrogen-ion concentration in a solution. A single indicator will tell us only whether the $[H^+]$ is greater than, less than, or about the same as its $K_a$ value. You select the indicator according to the pH where you would like to see a color change. For example, phenolphthalein has a pKa of 9.2. We would expect to see a color change in a solution having a pH of about 9. The two forms of phenolphthalein are shown below.




Colorless Red

Sodium hydroxide is hygroscopic and absorbs water from the air when you place it on the balance to measure its mass. This water will prevent you from being able to find the exact mass of sodium hydroxide. In order to determine the exact concentration of a sodium hydroxide solution you must standardize it by titrating with a solid acid that is not hygroscopic. Potassium hydrogen phthalate, $KHC_8H_4O_4$ (abbreviated KHP), is a non-hygroscopic, crystalline, solid that behaves as a monoprotic acid. It is water soluble and available in high purity. Because of its high purity, you can determine the number of moles of KHP directly from its mass and it is referred to as a primary standard. You will use this primary standard to determine the concentration of a sodium hydroxide solution. The structure of KHP is shown below:



When KHP and a base a reacted, a neutralization reaction occurs that is represented by the following equation:

$$KHC_8H_4O_{4\,(aq)} + NaOH_{(aq)} \rightarrow KNaC_8H_4O_{4\,(aq)} + H_2O_{(l)}$$

The net ionic equation is:

$$HC_8H_4O_4^{-1}{}_{(aq)} + OH^-_{(aq)} \rightarrow C_8H_4O_4^{-2}{}_{(aq)} + H_2O_{(l)}$$

The reaction can be considered to proceed completely to the right. If exactly equivalent amounts of acid or base are used so that neither reactant is present in excess the solution is said to be at the **equivalence point**. If only monoprotic acids and bases are used (those that react with one $H^+$ per molecule), then at the equivalence point the number of moles of acid equal the number of moles of base (moles acid = moles base).

**Experiment equipment/materials**:

| | |
|---|---|
| Bottles | Hot plates |
| 250 mL Erlenmeyer flasks | Buret |
| 1 L beaker | Phenolphthalein indicator |
| 50 mL graduated cylinder | 0.1 M NaOH solution (prepared by students) |
| Plastic pipet | Primary standard KHP |
| (1:1) NaOH saturated solution* | Unknown samples |
| Distilled water | |
| *(1:1) saturated NaOH solution: the solution is usually prepared by mixing 50 g of sodium hydroxide pellets with 50 mL of water in a polyethylene bottle. Let stand until sodium carbonate has settled | |

P**rocedure**

1. Prepare the NaOH solution with about 0.1 M concentration as follows:
   a. Using 1 L beaker, boil about 1 L of distilled water for 5 minutes to remove any dissolved carbon dioxide
   b. Remove the beaker from the heat sources, cover it with a watch glass and allow the water to cool to about 40 $^oC$
   c. Transfer the warm water to a polyethylene 1 L bottle with a rubber stopper
   d. Transfer about 7 mL of a clear saturated (1:1) solution of sodium hydroxide the bottle using a transfer pipet
   e. Mix thoroughly and keep covered
2. Standardize the 0.1 M NaOH as follows:

a. Perform rough titration: weigh accurately (to within 0.0001 g) between 0.7xxx and 0.8000 g of KHP (MW = 204.23 g/mol) with no more than 0.8000 into a 250 mL Erlenmeyer flask by difference. **Note:** If the mass of KHP taken exceeds 0.8000 g, the titration may require more than 50 mL of titrant, making it necessary to refill the buret and thereby introducing two more buret reading errors.
b. Add about 50 mL water using 50 mL graduated cylinder to the KHP. Swirl the flask and rinse down the sides of the flask to dissolve the sample. (Remember - we are concerned only with the amount, in moles, of acid; the exact volume is not important)
c. Add 3 or 4 drops of phenolphthalein indicator to the flask.
d. Obtain a buret, wash it with water and soap, then rinse it 2 or 3 times with small portions of the NaOH solution before filling it with it. Make certain that all air bubbles have been flushed from the tip before taking the initial volume reading. When reading the buret, remember that you should **read** the number that is at the bottom of the meniscus and estimate each reading to the closest 0.01 mL.
e. Titrate the sample of KHP until the faint, pink endpoint is reached. Add the NaOH titrant rapidly at first, but slowly later as the endpoint is approached as indicated by the less rapid disappearance of the pink color as the added titrant mixes with the solution in the flask. Rinse down the sides of the flask to make sure that any splattered NaOH get a chance to react. Add the final increments dropwise, or even in half-drops washed from the buret tip with a few drops of water. The endpoint has been reached when a faint pink color persists throughout the mixed solution for about 30 seconds. (**Note:** dissolving $CO_2$ will produce carbonic acid, which will neutralize the excess NaOH and turn the phenolphthalein colorless if the titration too far overrun). Exercise care to avoid overshooting the endpoint (intense pinkish-red color). If you do accidentally overshoot the endpoint, weigh a fresh sample of KHP and repeat the titration.

3. **Perform accurate titration**: based on the volume of NaOH used in step 2 above, **calculate** the amount of KHP needed for at least 40 mL by multiplying the weight you used in step 2 above by the ratio 40 ml / volume of NaOH used. For example, if you used 25.00 mL to titrate 0.7900 g KHP, then you should weigh 0.7900 g * (40.00 mL/25.00 mL) = 1.2600 g KHP
4. Weigh the KHP amount based on your calculation in step 5 above into each of three 250 mL Erlenmeyer flasks and prepare each of the samples for titration as in steps 2 (b-e) above and record the volume of NaOH needed to two decimal digits.
5. **Calculate** the moles of KHP, moles of NaOH and the molarity of the NaOH. Average the molarities from the three different trials and calculate the standard deviation, G-test and 95% confidence interval.
6. **Determination total acidity of an unknown**: obtain an unknown from your TA/lab instructor and record its letter
7. Weigh out 1.0xxx gram of the unknown into a clean 250 ml Erlenmeyer flask and add 50 ml of water and 2 or 3 drops of phenolphthalein. Titrate the unknown as rough titration and record the NaOH volume needed to reach the end point
8. **Calculate** the amount of unknown (in gram) needed to titrate at least 40 mL of NaOH as in step 5 above
9. Weigh the calculated amount of the KHP unknown sample into each of three 250 mL Erlenmeyer flasks and prepare each of the samples for titration as in steps 2 (b-e) above and

record the volume of NaOH needed to two decimal digits. (NOTE: *Do not discard the remaining NaOH – you will use this for other experiments).*

10. **Calculate** the moles of KHP, grams of KHP and determine the % KHP in the unknown and the average % mass KHP from the three different trials and calculate the standard deviation, G-test and 95% confidence interval.

**Data table 1: Standardization of a NaOH solution with standard potassium hydrogen phthalate (KHP)**

| | Trial 1 | Trial 2 | Trial 3 |
|---|---|---|---|
| Mass of KHP (g) | | | |
| Initial buret reading (mL) | | | |
| Final buret reading (mL) | | | |
| Volume of NaOH used (mL) | | | |
| Volume of NaOH used (L) | | | |
| Moles of KHP | | | |
| Moles of NaOH | | | |
| Molarity of NaOH | | | |
| Average Molarity of NaOH | | | |
| Standard deviation in the NaOH molarity | | | |
| 95 % confidence interval | | | |

**Sample calculation: (show one sample calculation for each of the reported data—use additional paper if needed)**

**Data table 2: determination total acidity as (KHP) in an unknown sample**

| Unknown letter: _____ | Trial 1 | Trial 2 | Trial 3 |
|---|---|---|---|
| Mass of unknown (g) | | | |
| Initial buret reading (mL) | | | |
| Final buret reading (mL) | | | |
| Volume of NaOH used (mL) | | | |
| Volume of NaOH used (L) | | | |
| Molarity of NaOH (M) | | | |
| Moles of NaOH | | | |
| Moles of KHP | | | |
| Mass of KHP (g) | | | |
| % mass of KHP in unknown _____ | | | |
| Average % mass of KHP in unknown _____ | | | |
| Standard deviation in the % mass of KHP | | | |
| 95 % confidence interval | | | |

**Sample calculation: (show one sample calculation for each of the reported data—use additional paper if needed)**

## Example calculations:

Let's assume 0.5472 g of 100% pure KHP is titrated with a NaOH solution of which the molarity is not known to 4 significant figures. The following equation is used to calculate the molarity of the NaOH solution.

Assume 37.42 mL (0.03742 L) of sodium hydroxide were used to titrate the KHP. Therefore:

0.5472 g KHP/1 x 1 mol KHP/204.23 g KHP x 1 mol NaOH/1 mol KHP x 1/0.02742 L NaOH = 0.09771 mol NaOH/1 L NaOH.

Assume we used 25 ml of NaOH to reach the endpoint using 0.1000 mol/L NaOH. To calculate the moles of acid the following formula is used:

0.1000 mol/L NaOH x 0.02500 L NaOH x 1 mol HA/1 mol NaOH = 0.0025 mol HA

Further, assume HA represents KHP. To determine the percent KHP in an unknown sample mass of 0.9735 g, the following calculation is used:

0.0025 mol KHP x 204.23 g KHP/1 mol KHP x 1/0.9735 g unknown x 100% = 52.44% KHP

**Pre lab: Standardization of NaOH and determination of total acidity as KHP**

**Name_____ ID_____**

**Partner name_____ Date_____**

1. A 0.8234-g sample of "KHP" required 38.76 mL of NaOH for titration to the phenolphthalein endpoint. What is the exact molarity of the NaOH solution?

2. A 25.00-mL aliquot of an unstandardized HCl solution is titrated with the previously standardized NaOH solution from #1 above. If 32.55 mL of NaOH titrant is required to reach the endpoint, what is the exact molarity of the HCl solution?

3. Why is distilled water boiled before it is used in preparing sodium hydroxide titrant? Write the chemical reaction that occurs when unboiled distilled water is used.

4. Why should the sample size be such that not more than 50 mL of titrant is required to reach the endpoint?

5. What mass (in grams) of "KHP" should be used for the standardization of a NaOH solution that is approximately 0.14 M NaOH if the volume of NaOH titrant used is to be about 45 mL?