Chemistry 3200
Determination of Mixed Acids

Acid-base titration is one of the most common operations in analytical chemistry. A solution containing an unknown amount of ionizable hydrogen can be titrated with a solution of standard base until all the hydrogen ion has been consumed according to the following reaction:

\[ H_3O^+ + OH^- \rightleftharpoons 2 H_2O \]

From the known concentration and measured volume of the "standard base" the number of moles of unknown acid present can be readily calculated.

The determination of the equivalence point in an acid-base titration (i.e., the point at which the number of moles of OH\(^-\) added to the titration vessel is equal to the number of moles of ionizable H\(_3\)O\(^+\) present) is usually relatively easy. If one were to plot pH versus volume of base added for the titration of a strong acid with strong base, a very abrupt change in pH at the equivalence point would be observed. The change in pH may be observed visually by the addition of an indicator. You will perform an acid base titration using both of these methods in this lab. An acid-base indicator is a weak organic acid, usually with a complicated formula that will be abbreviated as HIn. The indicator can exist as the acid form, HIn, or as the base form, In\(^-\). These two forms have different colors. When the pH of the solution changes from comparatively acidic to comparatively basic in the course of a titration, the indicator changes from predominantly HIn to predominantly In\(^-\) because the equilibrium shown below is shifted to the right.

\[ HIn \rightleftharpoons H^+ + In^- \]

Sodium hydroxide (NaOH) is commonly used as a standard base solution. However, NaOH is not a primary standard (a substance of exactly known purity which can be readily weighed to provide a known amount of reactant) because the solid NaOH readily absorbs CO\(_2\) and water. Sodium hydroxide solutions are usually prepared by first preparing a 50 % solution of NaOH, allowing any Na\(_2\)CO\(_3\) to precipitate (Na\(_2\)CO\(_3\) is quite insoluble in 50 % aqueous NaOH solution) and more dilute NaOH solutions prepared by dilution of the 50 % NaOH solution with water purged of CO\(_2\) (i.e., freshly boiled water). The dilute NaOH solution is ordinarily standardized against potassium hydrogen phthalate (KHP), a readily purified solid acid of high formula weight having the following structural formula:

![KHP Structural Formula](image)

The formula weight of KHP is 204.23. Since it has only one ionizable hydrogen ion the equivalent weight is the same as the formula weight.
Sodium hydroxide solutions rapidly absorb CO\(_2\) from the air and must be protected from exposure to the atmosphere if stored. When NaOH is used as a titrant, it is best to standardize the solution (i.e., determine its concentration using a chemical test) shortly before performing the analysis. Otherwise the concentration of NaOH may drop with time due to reaction with CO\(_2\). Stock solutions of NaOH can also be protected from the atmosphere by traps filled with Ascarite (an asbestos material coated with NaOH).

**Procedure** (Students will work in groups for this experiment)

**Standardization of NaOH**

1. Deliver ~8 mL of the 50% NaOH solution to a one-liter volumetric flask and dilute to volume with DI water. Stopper the bottle, and mix thoroughly. This will give an approximately 0.1 M solution of NaOH.
2. The KHP used to standardize the NaOH solution must be dried for 1 h at 100 °C. Dried KHP will be provided. Weigh four ~0.7 g portions of pure dried KHP into four separate 250 mL Erlenmeyer flasks. The portions do not need to be exactly 0.7 g, but you must record the exact mass used. Record each mass to 4 decimal places. Dissolve the KHP in each flask in approximately 50 mL of DI water and add 2 drops of phenolphthalein indicator.
3. Calculate the approximate volume of NaOH required for each titration by assuming that the NaOH solution is 0.1 M.
4. Perform a rough titration with the first sample to find the approximate volume needed for the more careful titrations by adding NaOH titrant while swirling the contents of the flasks until the first perceptible pink color appears that persists for several seconds. Note: the pink color should **not** be the intensity of raspberries. Complete the titrations reasonably rapidly because CO\(_2\) may be absorbed from the atmosphere from basic solutions and the endpoint may fade if you are too slow.
5. Titrate the remaining KHP standard samples.
6. Perform blank titrations. A blank is prepared identically to the KHP samples, but without the KHP. (i.e., prepare a sample containing 50 mL DI water and 2 drops of indicator, and titrate it.) The titration should only require a drop or two. If it is hard to read the titrant volume from the buret due to small change, measure the number of drops of NaOH solution in 1 mL of titrant, and calculate the volume of a drop. Correct your titration volumes by subtracting the volume required to titrate the blank.
7. Calculate the molarity of the standard NaOH. If the average relative deviation on your three samples exceeds 3 parts per thousand, you should weigh out some more solid KHP and repeat the standardization. If the molarity of your standard sodium hydroxide varies by more that 20% from the 0.1 M target, you may want to make a new solution. Consult your lab instructor in this case. Re-standardization will be necessary if you have to change the concentration of the NaOH.
Calibration of the pH Meter (Model: Fisher Scientific accumet® AE150)

You will follow this titration using pH meter and indicators for comparison. Accurate use of a pH meter requires pH readings after addition of every 0.5 to 1 mL when far from the endpoint, but readings must be taken after every drop near the endpoint. Before preparing your sample you must standardize your pH meter. Make sure that the meter is plugged in and turned on before you begin.

1. The pH meter is in the measurement mode once it is turned on. You should see MEAS on the display.
2. Press the “CAL/MEAS” button to change to the calibration mode. You should now see CAL shown on the display.
3. Rinse the electrode with DI water and blot dry with a lint free Kimwipe, or gently shake dry.
4. Immerse the pH electrode into pH 7 buffer solution. Once the reading is stable, press “ENTER”.
5. Repeat steps 3 and 4 to calibrate with pH 4 and pH 10 buffers.
6. Once the pH meter is calibrated with all three buffer solutions, it will automatically change to the measurement mode. The pH meter is now standardized.

Titration of a HCl–H₃PO₄ Mixture Using Indicators and a pH Meter

1. Pipet 25.00 mL of an unknown solution containing a mixture of HCl and H₃PO₄ into a 250 mL volumetric flask. Dilute the contents of the flask to the mark, using a medicine dropper for the last several drops, and mix.
2. Pipet a 25.00 mL aliquot of the diluted acid mixture into a 400 mL beaker and add 200 mL of water.
3. Add 1 drop of methyl orange indicator and 12 drops of thymolphthalein indicator.
4. Rinse the electrode and place it in the unknown acid solution that is set up for stirring with a magnetic stirrer. The glass electrode used for measuring pH is a fragile device and should be handled with care.
5. Determine pH as a function of the volume of NaOH. Add the NaOH in 1 mL increments and record pH versus volume of NaOH. This is a rough titration to show you the locations of the two equivalence points and may be done rapidly. Make sure to record the pH at which each indicator goes through a color change for each titration. The volume at color change will be qualitative. The pH meter will give better results.
6. Perform three additional titrations in which readings are taken at ~0.1 mL intervals around the equivalence points (this can be done by adding 2 drops at a time, since the drop volume is now known) and at 1 mL intervals elsewhere.
7. Record volume and pH data in your lab notebook. This can be done easily in the spreadsheet.

Analysis will be done using a spreadsheet such as Microsoft Excel. Enter the volume and pH data into the spreadsheet. Indicate the pH where each color change occurs. Plot the pH versus corrected volume of titrant for each titration.
Make a derivative plot of the data as instructed by your lab instructor. Determine the volume of NaOH at the 1\textsuperscript{st} and 2\textsuperscript{nd} equivalence points by locating the inflection points of the curve.

**Reporting Results**

Report total moles HCl and total moles H\textsubscript{3}PO\textsubscript{4} in your sample as determined from the titrations using indicator and total moles HCl and total moles H\textsubscript{3}PO\textsubscript{4} from the potentiometric titration. The total moles of HCl plus H\textsubscript{3}PO\textsubscript{4} are obtained from the volume of NaOH required to reach the first equivalence point (the methyl orange endpoint). The additional volume of NaOH required to reach the second equivalence point (indicated by the thymolphthalein indicator change) gives the moles of H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} present. Because all the H\textsubscript{3}PO\textsubscript{4} initially present was converted to H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} by the base added prior to the first equivalence point, the moles of base added between the first and the second equivalence points gives the moles of phosphoric acid in the sample. This is subtracted from the moles of base used to reach the first equivalence point to obtain the moles of HCl originally present. The total moles of HCl and H\textsubscript{3}PO\textsubscript{4} initially present will be \sim 10 times the amount obtained in your titration as you are taking a 25 mL (your pipet volume) aliquot from the 250 mL volume that contains your entire sample.
**Chemistry 3200**  
**Determination of Mixed Acids**

Date: __________  Lab Instructor: ________________  Section: ________  
Unknown Number: ________

**Standardization of NaOH**

Blank volume: __________

<table>
<thead>
<tr>
<th>Grams of KHP</th>
<th>mL NaOH at endpoint</th>
<th>Corrected titration volume</th>
<th>Molarity of NaOH</th>
<th>Average molarity NaOH</th>
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<td>____________ ± ____________</td>
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**Unknown Titration**

<table>
<thead>
<tr>
<th>Volume of NaOH to 1\textsuperscript{st} endpoint</th>
<th>Volume of NaOH to 2\textsuperscript{nd} endpoint</th>
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<table>
<thead>
<tr>
<th>Average number of mL NaOH to 1\textsuperscript{st} endpoint</th>
<th>Average number of mL NaOH to 2\textsuperscript{nd} endpoint</th>
<th>Difference in endpoint volumes</th>
<th>First endpoint volume minus difference in volumes</th>
<th>Concentration of HCl in 250 mL sample</th>
<th>Concentration H\textsubscript{3}PO\textsubscript{4} in 250 mL sample</th>
<th>Concentration of HCl in original sample</th>
<th>Concentration H\textsubscript{3}PO\textsubscript{4} in original sample</th>
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<td>____________ ± ____________</td>
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*Attach graphs of three titrations and the derivative plots.*  
*Indicate the equivalence points and note the indicator color changes.*

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**Determination of Mixed Acids**
Calculation of HCl concentration in unknown:

Calculation of H$_3$PO$_4$ concentration in unknown:
Calculation for error analysis (Include a list of the errors and their sources):