

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Department of Chemistry
5.310 Laboratory Chemistry

EXPERIMENT #5

THE POTENTIOMETRIC TITRATION OF AN ACID MIXTURE¹

I. PURPOSE OF THE EXPERIMENT

In this experiment the quantitative composition of a solution, which is a mixture of a monoprotic strong acid and a weaker triprotic, acid will be determined by potentiometric methods. This experiment will introduce you to quantitative volumetric analysis and potentiometric titrations.

- (A) A carbonate-free sodium hydroxide solution is prepared and standardized against pure potassium hydrogen phthalate (KHP), and is then used in a potentiometric titration of the acid mixture.
- (B) Three or four 1.0 mL aliquots of your acid will be used for potentiometric titrations. Each titration must be continued through two equivalence points.

II. INTRODUCTION

Strong acids, like hydrochloric acid, are completely dissociated in water, but weak acids, like acetic acid, are only partially dissociated. The extent of dissociation can be calculated from the value of the equilibrium constant and the amounts of weak acid and strong base added to the solution.

The relative acidities of acids and bases are commonly expressed in terms of $pK_a = -\log_{10} K_a$, where K_a is the dissociation constant for the reaction



In the following derivation, a_{A^-} , $[A^-]$, and γ_{A^-} represent, respectively, the activity, the molar concentration, and the activity coefficient of the conjugate base, A^- .

$$K_a = \frac{(a_{H^+})(a_{A^-})}{(a_{HA})} = \frac{[H^+][A^-]}{[HA]} * \frac{(\gamma_{H^+})(\gamma_{A^-})}{(\gamma_{HA})}$$

Since $pK_a \equiv -\log K_a$

¹ Adapted for microscale quantities by M. D. Gheorghiu. The experiment includes contributions from past instructors, course textbooks, and others affiliated with course 5.310.

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$$\text{then } pK_a = -[\log(a_{H^+}) + \log(a_{A^-}) - \log(a_{HA})]$$

$$\text{since } pH \equiv -\log(a_{H^+})$$

$$\text{then } pK_a = pH + \log(a_{HA}) - \log(a_{A^-})$$

$$pK_a = pH - \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

$$pK_a = pH - \log\left\{\frac{[A^-]}{[HA]} \times \frac{[\gamma_{A^-}]}{[\gamma_{HA}]}\right\}$$

Making the approximation that $\frac{[\gamma_{A^-}]}{[\gamma_{HA}]} \cong 1$

yields an apparent $pH = pK_a + \log([A^-]/[HA])$.

This equation is referred to as the Henderson-Hasselbalch equation. It is very useful in the buffering region of the titration of a weak acid. The pK_a is $-\log K_a$ at the ionic strength of the solution. Accordingly, the value of K_a obtained will deviate slightly from values listed in standard references since they report the thermodynamic value at zero ionic strength.

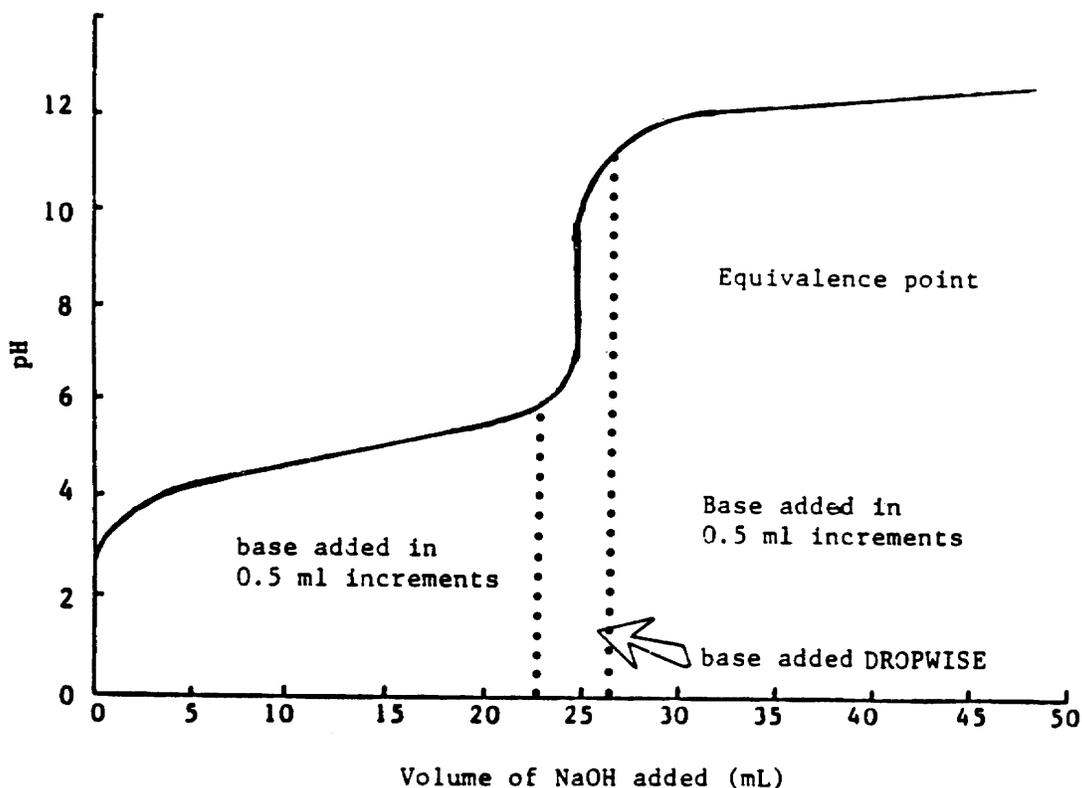
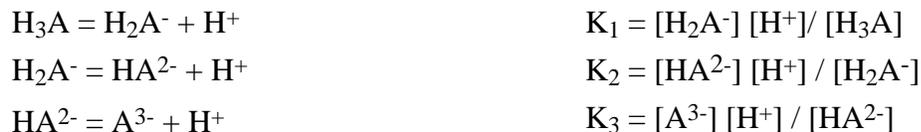


Figure 1. Typical Plot of a Potentiometric Titration to Determine the Equivalence point and pK_a value (monoprotic acid)

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Note that the pK_a is the pH at which the activities of the acid HA and its conjugate base A^- are equal.

For a triprotic acid the successive dissociation constants are defined by:



The normality of an acid solution is the number of equivalents per liter (moles per liter) of protons that it can dissociate. The normality of a solution of a base is equal to the number of equivalents of acid it can neutralize. The normality of a solution of a triprotic acid is three times its molarity. In discussing titrations of acid and base solutions, it is often convenient to think in terms of milliequivalents.

III. SAFETY

You will handle several chemicals during this experiment; some that must be treated with care in order to avoid damage to yourself or your surroundings. None of these chemicals should be ingested. You should also avoid contact with them on your skin or your eyes. The chemicals are described in this section and denoted by an asterisk when they are first used in the experimental procedure.

1. **Sodium hydroxide** (NaOH) 50% w/w: conc. NaOH is very caustic and should be handled with care. Avoid spilling it on your hands or clothing. If NaOH gets on your skin, rinse immediately with plenty of water.
2. **Hydrochloric acid** (HCl): Avoid contact of acid with skin or clothing. Dilute HCl is used in this experiment, and is less hazardous than concentrated HCl. If HCl is spilled on your skin or clothing, remove clothing immediately and use plenty of cold water to rinse skin.
3. **Calcium chloride** ($CaCl_2$): hygroscopic salt that is not particularly hazardous in small quantities. It is used on roads along with NaCl to prevent icing and is hazardous to cars over the long term. This salt is used in the laboratory in desiccators to keep solid samples dry. Rinse with water if calcium chloride is on your skin.
4. **Potassium hydrogen phthalate**: KHP is a PRIMARY STANDARD. It is a monoprotic acid salt, not particularly hazardous. Handle with the usual precautions. Do not ingest. (FW=204.23)
5. **Phenolphthalein**: This chemical is an organic dye that is toxic in large quantities. It should be handled with the usual precautions: do not ingest, get on your skin or eyes, and do not spill into the laboratory environment.

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6. **Phosphoric acid** (H_3PO_4): Concentrated solutions are irritating to the skin and mucous membranes. Essentially nontoxic, it is used to flavor foods and in other commercial applications.

General References

- Review of Chemical Units of Weight and Concentration and Stoichiometry **SWH** pp. 64-72
- Primary standards, end points and equivalence points, standard solution **SWH** pp. 94-96
- Calculation of concentration of standard solutions and results of titrations **SWH** pp. 97-107
- Activity and Activity Coefficients **SWH** pp. 149-156
- Indicators for acid-base titrations **SWH** pp. 212-218
- Preparation of standard solutions of base **SWH** pp. 266-268
- Determination of Dissociation Constant **SWH** pp. 436-437
- Precision Weighing and desiccation **TM** 6:4-11,
- Manipulation of Weighing bottles **SWH** pp. 806-808
- Ordinary titrations **TM** 8:6-7
- Titrations sensitive to atmospheric interference (CO_2) **TM** 8:8-9
- Omission of Activity Coefficients in Equilibrium Calculations **SWH** pp. 156
- Titration Curves of Weak Acids **SWH** pp. 224-229
- Potential Measurements, pH meters **SWH** pp. 432-437
- Silver-silver chloride electrodes **SWH** pp. 402-403
- Glass electrodes for pH measurement **SWH** pp. 406-414
- Activity vs. Concentration **SWH** pp. 146-147
- Potentiometric pH Measurements with Glass Electrode **SWH** pp. 406-414
- Standardization of NaOH against KHP **SWH** pp. 846-847
- The Determination of Dissociation Constant **SWH** pp. 437-439

Videos: Digital Laboratory Techniques Manual

- #1. Volumetric Techniques (pipet, buret)
- #2. Titration
- #3. Balances

IV. PROCEDURE

1. Preparation of 0.05 M sodium hydroxide*

The TAs will prepare a solution of approximately 0.05 M NaOH as follows: Put 2.00 L of distilled water into the one gallon polyethylene bottle.² Measure out 5.5 mL of 50% w/w NaOH* in a 10 mL graduate cylinder and pour into the water in the bottle.³ Both the solution bottle and 50% NaOH bottle should be closed immediately with their polyethylene screw caps. Mix the dilute sodium hydroxide solution very thoroughly by vigorous shaking with repeated inversions for at least a minute.⁴

Day #1:

2. Standardization of Approximately 0.05 M sodium hydroxide (when two groups are performing this experiment one group will do this on day #2)

Place 100 mg of reagent grade potassium acid phthalate* (KHP) into a dry weighing bottle, and place in a 110 °C drying oven for 1.5 hour or overnight.⁵

At the end of the drying period, remove the weighing bottle from the oven and let cool in a small desiccator charged with calcium chloride*. Leave the stopper off of the weighing bottle until the first time the desiccator is opened after the KHP has cooled. Observe the precautions involved in the use of desiccators mentioned in Chapter 6 of the Techniques Manual.

Weigh by difference at least three samples of KHP into numbered or otherwise identified 25-mL Erlenmeyer flasks. Sample weights should be 30 mg for the primary standard. Estimate all weights to ± 0.1 mg (0.0001 g) and record all data immediately in the notebook.

Dissolve the KHP samples by swirling in 7 mL of water. Warming may be necessary. It is essential that the samples dissolve completely; even a few small particles remaining can cause a serious titration error.

² Many textbooks recommend boiling water beforehand to remove dissolved CO₂. In practice this is only necessary if very dilute solutions of NaOH are to be prepared (0.01M or less).

³ Solid sodium hydroxide is always coated with sodium carbonate and is not suitable for making up these solutions. Na₂CO₃ is virtually insoluble in very concentrated NaOH so that dilution of the unshaken 50% reagent is a very convenient way of obtaining carbonate free base. Concentrated NaOH will dissolve human skin.

⁴ It is always important to mix a standard solution very thoroughly and it is surprising how much mixing is necessary. Unless this is done, significant differences in concentration can persist and cause lack of agreement in subsequent titrations. In the present instance, the dense, viscous concentrated hydroxide solution needs to be dispersed throughout the solution by repeatedly inverting the bottle and shaking vigorously. This procedure should be repeated every time you prepare to take out additional NaOH.

⁵ Potassium acid phthalate is available in high purity and makes an excellent primary standard for alkalimetry where phenolphthalein is used as the indicator. The purpose of the drying period is to remove superficial moisture.

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Add 1 drop of phenolphthalein* indicator and titrate with the sodium hydroxide solution from a 10 mL buret. (tolerance ± 0.02 mL). On the lower end of the buret attach a disposable 1-200 μL plastic tip. The plastic tip helps in the formation of small droplets of solution to drop from the buret. Use parafilm to secure the tip of the buret.

Each time you fill the buret with fresh solution, rinse the buret 3 times with 2 mL of the new solution, discard each wash. Tilt the buret to allow the entire inner surface of the buret come into contact with the liquid. After rinsing out the buret, fill it with the NaOH solution. Expel air bubbles trapped below the stopcock by fully opening the stopcock a second or two. If this is unsuccessful see your TA for additional advice.

The titration may be carried out rapidly at first, but the endpoint should be approached carefully. With low-carbonate NaOH, the endpoint should be sharp and easily located to within a fraction of a drop.⁶ Try to obtain the same intensity of pink color at the endpoint for all your titrations. At the endpoint, the ideal indicator color is a barely detectable shade of pale pink which persists for 30 seconds or more.

Make all buret readings by estimating the nearest 0.01 mL, allowing time for drainage. The tendency of liquids to stick to the walls of the buret can be diminished by draining the buret gradually. A slowly drained buret will also provide greater reproducibility of results. Run a sufficient number of titrations to assure a precise and presumably accurate standardization. The standardization titration should be repeatable to within 2 to 3% when volumes of about 1.5 mL of base are used.

If three titrations do not result in the desired precision, it will be necessary to conduct additional titrations. With your notebook pages turned in at the end of the day, include a table giving the calculated normality of the NaOH from each titration, the average and the 95% confidence limits of the mean. Estimate what you think the uncertainty is in weighing, using the buret, and in endpoint location. Do error propagation from these values and compare with the observed precision.

Record your calculated normality for each titration on your TAs class data sheet **before** leaving the lab for the day.

⁶ The phenolphthalein endpoint is taken as the first distinct pink color that persists for 10 seconds or more after thorough mixing. The color is not permanent but will fade in a matter of minutes or less as a result of absorption of CO_2 from the air.

Day #2: Titration of a Mixture of Hydrochloric Acid* and Phosphoric Acid*

(see Appendix 1)

(When two groups are performing this experiment, one group will do this on day #1)

You will be given a mixture of these acids.* Your goal is to report the molarity of the hydrochloric acid and the molarity of the phosphoric acid in the mixture, with their uncertainties. You will also determine the value of pK_2 for the phosphoric acid.

Using a VOLUMETRIC PIPET, pipet 1.00 mL of the acid mixture into a 30-50 mL beaker and add 19.0 mL using graduated pipets of distilled H_2O . Note that volumetric pipets are NOT designed to be blown out, allow it to drain naturally then touch the tip of the pipet just to the surface of the solution drained. This pipet is calibrated for a small quantity of solution to remain in the tip. Place a magnetic stir bar in the beaker.

Rinse the pH electrode with distilled water into an empty beaker and p Position the electrode and 10 mL buret filled with sodium hydroxide as indicated in Figure 3. Be sure that the pH electrode is not in a position to be damaged by the magnetic stir bar.

No air bubbles should be trapped under the polyethylene shield of the electrode. Also, make sure that no air bubble is trapped in the tip of your buret.

Insulate the beaker from the magnetic stirrer with a layer of folded paper towel to prevent warming of the solution by the magnetic stirrer.

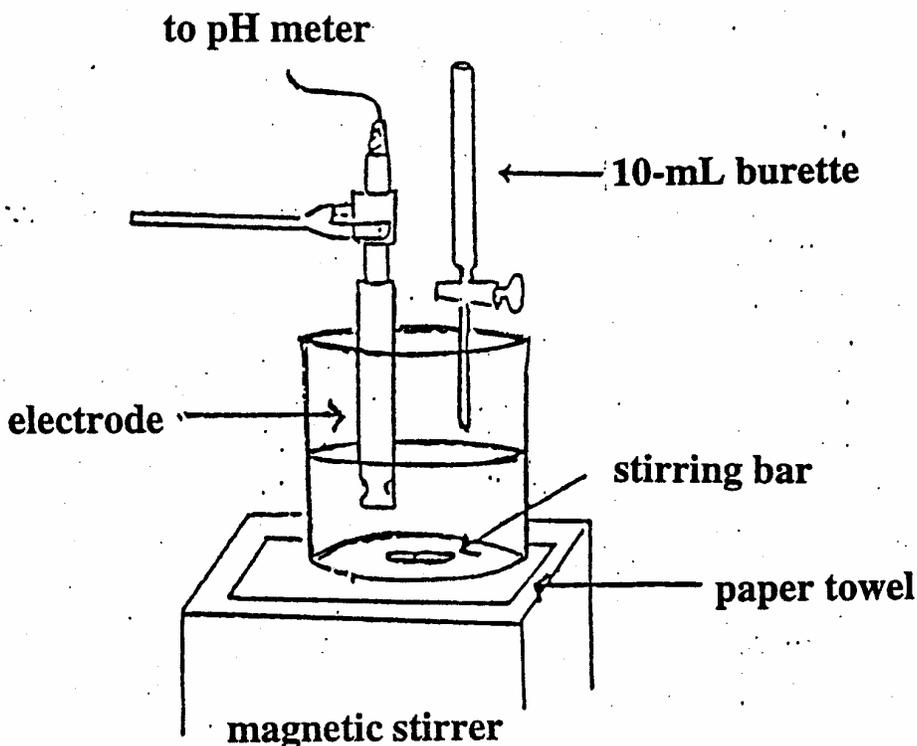


Figure 3. Titration apparatus

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With continuous stirring, add small increments of the approximately 0.05 M standard solution of NaOH from the buret. Give the solution and pH meter time to equilibrate. Read and record in the notebook the pH of the solution after addition of each portion of the NaOH solution. Initially, the change of pH upon the addition of titrant will be minimal. However, as the first equivalence point is approached, pH increments will increase more rapidly, and only dropwise increments of NaOH should be added until it is apparent that the first equivalence point has been passed.

Periodically the inside of the beaker may be washed down with distilled H₂O from your water bottle.

Warning: Be sure no drops are left on the tip of the buret when you are reading the pH. The drop is part of the measured volume. You will not have good correlation between volume and pH if part of the volume measured is left out. This is especially important in the regions of rapid pH change.

Do not take pH readings above pH 11.5, because high pH damages the glass electrode.

After the first potentiometric titration, remove the electrode from the solution, wash it with distilled water and allow the electrode to stand in a beaker of distilled water for at least 15 minutes before proceeding with the second titration. It is a good procedure to check the calibration of the meter against a standard aqueous buffer of pH 7.0 before beginning another titration.

While waiting, plot your data by hand or use your PC. Review your titration curve with your TA. Discuss any changes which should be made for subsequent titrations.

Day #3:

Bring your analysis of your titration data to the laboratory. If you are not satisfied with your data discuss your concerns with your TA before carrying out additional titrations.

V. DATA ANALYSIS AND DISCUSSION-REQUIRED

Analyze the data from your titrations with Microsoft Excel as it is described in the lecture handouts.

All the questions below should be discussed in your report.

1. Plot your experimental data as *pH* versus *volume of standard NaOH added*. Use a full sheet of graph paper for maximum accuracy and draw a smooth curve through the points.
2. For each titration identify the two equivalence points and draw vertical lines to determine the corresponding volumes of NaOH. The portion of the titration curve between the two equivalence points should follow the Henderson-Hasselbalch equation.

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3. Calculate the pK_{a2} for H_3PO_4 , and **test the validity** of the Henderson-Hasselbalch equation by calculating several other points on this part of the titration curve.

- a. How does your pK_{a2} value compare with the literature value?
- b. Your titration does not yield values of pK_{a1} and pK_{a3} but something can be said about these pK_a values from your experimental data. What is it?
- c. Since the titration will most likely not continue through pK_{a3} , how does its value depend the shape of the curve at the point where the titration ends if pK_{a3} is approximated by extrapolation?

4. From the sample volume and the distances to the first and second equivalence points, calculate the **MOLARITIES** of hydrochloric and phosphoric acids in the sample. **Give uncertainties for the calculated molarities. How well do your two or three titrations agree?**