

## Experiment # 8: Qualitative pH titration curves

Procedures involving pH measurements are among the most common analytical techniques. The acidic or basic properties of a compound are important characteristics of the substance and may influence the kinetics or equilibrium systems of chemical and/or physical reactions. Solution pH and pH changes are routinely measured by one of two methods: visual indicators or pH meters. Since most indicator color change intervals cover 2 pH units or more, pH meter (i.e., potentiometric) measurements are inherently more precise and accurate. In addition, it may not be possible to obtain an appropriate indicator, making it necessary to measure pH by potentiometric methods.

A pH meter is actually a high-impedance voltmeter which measures the potential difference between two electrodes or half-cells: a reference electrode (of saturated calomel or Ag/AgCl) of constant potential and a pH indicator electrode (usually having a special glass membrane sensitive to hydrogen ions). The potential of the indicator electrode varies according to the Nernst equation, as:

$$E_{\text{ind}} = E_{\text{ind}}^{\circ} - 0.059 \log (1/ [\text{H}^+]) = E_{\text{ind}}^{\circ} - 0.059 \text{ pH}.$$

Thus, changes in pH are represented by the changes in the potential of the glass electrode. A recent design innovation has resulted in the combination electrode, a one-piece unit containing both the indicator and reference electrodes in a single structure. (Read about the “glass pH electrode” in the lecture text.)

Graphical methods are used to achieve maximum useful pH data for the investigated chemical system. In an acid-base neutralization titration, the solution pH is plotted against the volume of added titrant. The titration curve of a strong or monoprotic weak acid titrated with a strong base is S-shaped, having two horizontal regions at different levels joined by a vertical section. The first horizontal section represents the slowly decreasing analyte concentration, the vertical region follows the change-over from analyte to titrant control of solution pH, and the latter horizontal portion shows the steadily increasing titrant concentration. The equivalence point is interpreted as that point on the curve at which the rate of change in pH is at a maximum. This point is usually midway along the vertical portion most nearly parallel to the pH axis.

In a potentiometric acid-base neutralization titration, the analyte may be either a strong or weak species (the titrant must be a strong species). If a strong analyte is used, the analysis provides mainly quantitative information based on the equivalent mass relationships. More extensive information is obtained from a potentiometric analysis of a weak species.

A pure weak acid, for example, can often be identified by its equivalent mass and the pH values of the half-neutralized solutions. The pH of the solution at 50% neutralization equals the pK<sub>a</sub> for the dissociation process: [acid] ↔ [H<sup>+</sup>] + [base]. The equilibrium constant for the above reaction is called the acid dissociation constant, K<sub>a</sub>, and the equilibrium concentration relationships are given by:

$$K_a = \frac{[\text{H}^+][\text{base}]}{[\text{acid}]} \quad \text{or} \quad \text{p}K_a = \text{pH} - \log \frac{[\text{base}]}{[\text{acid}]}$$

At 50% neutralization, the conjugate pair concentrations are equal (that is,  $[\text{base}] = [\text{acid}]$ ), and the above equation reduces to:

$$K_a = 10^{\text{pH} - \text{pK}_a} \text{ or } \text{pK}_a = \text{pH} \text{ at } 50\%.$$

If the unknown acid is monoprotic; data analyses are simple and direct. Polyprotic weak acids can be investigated in a similar manner, although the data interpretations are more complicated.

In conventional potentiometric titrations, the analysis is an exact quantitative one involving accurate measurements of reagent volumes, and the concentrations of all reagent solutions are exactly known. Measurements are typically taken to at least four significant figures. The experiment to be performed in the lab will be performed at a less-sophisticated level. Reagent solutions of approximately known concentrations will be used, however, titrant volumes (in milliliters) and pH values will be read to the nearest hundredth of a unit.

Qualitative pH titration curves will be constructed from the experimental data. A strong acid and a weak acid will be investigated to determine their equivalence volumes and relative  $\text{pK}_a$  values (in the case of the weak acid). These acids will exhibit different pH titration curves.

### Calibration of pH Meter

The pH meters in use in the freshman lab have digital output and three adjustments. Start by setting the temperature at room temperature, usually about 25 °C, by pressing the °C key and adjusting the 'Temperature' knob. Next, press the pH key on the meter and immerse the glass combination electrode in standard pH = 7 buffer. After a couple of minutes, adjust the 'OFFSET' knob until the display reads 7.00. Rinse the electrode with deionized water and blot dry with tissue (not paper towels) and place the electrode in standard pH = 4 buffer. After a couple of minutes, adjust the digital meter to read 4.00 with the 'SLOPE' knob. Be patient with this setting and allow the signal to settle in before your final adjustment.

### Measurement of pH titration curve

Obtain a 50.00-mL buret from under the hood. Fill the buret with the 0.10 M NaOH from the solution bottle on the storage shelf. This stock base is prepared by dissolving 4.00 grams of NaOH per liter of deionized water. Make sure the base solution meniscus lies exactly on the 0.0-mL mark on the buret. Place the buret in a clamp above the solution.

Select the weak mono-protic acid solution provided and record the name and pertinent information in Table I as Acid 1. Use a 100-mL graduated cylinder to measure 25.0 mL of the acid solution into a clean 150-mL beaker, and then add a 25.0-mL portion of deionized water. Mix the solution, and place a clean magnetic stir-bar in the beaker. Place the beaker and solution on the magnetic stirrer unit. Note: If magnetic stirrers are not available, you will have to stir with a glass stirring rod.

Insert the calibrated pH meter electrode into the acid solution, and press the pH key on the pH meter control panel. Leave the pH meter control on "pH" throughout the entire titration of the acid. Turn on the magnetic stirrer (if available), and adjust the stir-bar rotation rate to an appropriate level. Record the initial pH of the weak acid solution (and the corresponding titrant volume of 0.0 mL) in Table I.

Position the tip of the buret at the height of the beaker lip. Open the buret stopcock, run in a portion of base, and close the stopcock. Allow the solution to mix for a few seconds while stirring, and then record the solution pH as read on the pH meter scale. For the first 10 mL of added titrant, add the base in 1.0-mL portions. Thereafter, use 0.5 mL base additions to obtain enough data points to define the titration curve. Portions smaller than 0.5 mL will not appreciably improve the pH curve, except in the region very near the equivalence point.

Continue adding titrant until the solution pH is above 11. Go to a final titrant volume of at least 2.5 times the equivalence volume (for example, if the equivalence volume is 16.0 mL, add titrant to a total volume of at least 40.0 mL). Addition of this much titrant is routinely done to insure that the acid does not have a second equivalence point. Your acids (both weak and strong) will be mono-protic. When one acid has been analyzed, turn the pH meter off and then remove and clean the electrode (and stir-bar if present).

Select the strong mono-protic acid solution provided and record the name and pertinent information in Table I as Acid 2. Measure the pH titration curve for this strong acid as analyte versus aqueous sodium hydroxide as titrant using the same procedure that was followed for the weak acid.

Students should work in groups of two or three as specified by the instructor. Group size may be dictated by the number of pH meters available for use. Each student in the group should rotate through the experimental duties of operating the buret while stirring, reading the pH meter, and recording the pH vs. mL titrant.

Table 1 has three columns for data entry, one for Acid 1 and one for Acid 2. The third column is included in case your instructor wants you to titrate another weak acid (Acid 3).



## Data treatment and report

This experiment will require a three-page report. The first page should include a complete heading and a full, neat copy of the pH vs. mL base data from Table I. Be sure to report the particular acids for which the data were taken. The second page of the report will be a neat, well-prepared pH titration curve of the strong acid, including a complete heading and title. Page three is to be the pH titration curve for the weak acid.

The scales of the axes of the pH titration curve should be chosen to use the entire graph page for the actual pH vs. mL titrant data sets. Plot pH on the ordinate (short, vertical axis), using a scale which ranges from just below the minimum pH reading to just above the maximum pH reading. Plot mL of base titrant on the abscissa (long, horizontal axis), using a scale ranging from 0.0 mL to a value slightly larger than the maximum or total volume of the last pH reading.

Draw a smooth curve through the data points: do not play connect-a-dot. It is not necessary that every data point lie on the line. For all weak acids titrated with a strong base, the equivalence point should lie at a pH above 7 (due to the equilibrium reactions of the conjugate pair). Determine the pH of the equivalence point of the titration curve in the vertical region midway between the two horizontal regions. Visual inspection or graphical interpretation methods are both appropriate. Write the value of the equivalence point pH on the graph to the right of the equivalence point.

The half-equivalence point (at 50% neutralization) occurs at the titrant volume half-way between 0.0 mL and the equivalence volume (that is, for a titration with an equivalence volume of 16.0 mL, the 50% point will be at 8.0 mL). The pH on the titration curve at the 50% neutralization point equals the  $pK_a$  of the weak acid.

Draw a vertical line from the 50% neutralization point volume on the abscissa to the titration curve, and then draw a horizontal line from the curve to the pH axis to determine the  $pK_a$  value. Write the value of the  $pH_{50\%} = pK_a$  on the graph above the horizontal line and next to the pH axis.

Record the name, concentration, and other pertinent information about the acids on the pH titration curve graph and on the first page of the report. Also, record the equivalence volumes and  $pK_a$  values on both pages of the report.