3.14 Titration

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3.14.1 About the Module

- Course: Calculus I
- Partner Disciplines: Chemistry
- Required Technology: web browser, spreadsheet

3.14.2 Institutional and Course Contexts

- Type/size of institution: Small liberal arts university
- Size of Class: 28 or fewer
- Characteristics of Students: Undergraduates from diverse mathematical backgrounds. Some are first year students who took Precalculus or Calculus in high school, others came through Augsburg's Precalculus course.
- Mathematical Content: Applications and numerical approximations of 1^{st} and 2^{nd} derivatives, concavity, inflection points, and working with data.
- Purpose/Goal of the Module: This module is designed for students to see a logistic-like curve arising naturally from data measured in one of our chemistry lab courses, apply calculus concepts to identify significant points on the curve, and connect these points to the goal of the chemistry lab – identifying an *equivalence point* in the process of titration.
- After and Before: This module comes, by design, later in the semester when unrelated topics are covered. It assumes the knowledge of the 1^{st} and 2^{nd} derivative and their interpretations. The goal is to recall and apply the concept of concavity some time after students first learned it.
- Other Prerequisites: Familiarity with basic spreadsheet functions; computation of (average) rates of change from data.
- Inspiration for the module: Working with a chemist; using data obtained in chemistry labs; using calculus to identify the acid used in the titration.

3.14.3 Partner Discipline Background

Titration is a method of chemical analysis in which a reactive substance is slowly added to another substance, and some property of the combined substance is measured. It is a foundational piece of analytical chemistry. Almost any fast reaction can be used to analyze an unknown chemical for quantitative information such as its concentration or molar mass. In performing a titration, the chemist holds a known solution (titrant) of known concentration in a buret. The buret is an analytical piece of glassware that dispenses precisely known volumes. The titrant is added into a flask containing the unknown solution (analyte). A visual indicator or a pH probe is used to determine the end of the titration (stoichiometric equivalence) and beyond. Each titration produces a characteristic S-shaped plot of some aspect of the analyte vs. volume of titrant added.

Acid-base titrations take advantage of the rapid and complete reaction between an acid and a base. This reaction can be represented as

$$\mathrm{HA} + \mathrm{OH}^- \to \mathrm{H_2O} + \mathrm{A}^-,$$

where HA is the acid being titrated, OH^- is the base being added, and H_2O is the water and A^- is the salt, products of the reaction. The ratio of acid to base is one molecule of acid to one molecule of base (or scaled by Avagadro's number, one mole of acid to one mole of base). Equivalence in the reaction occurs when the number of moles of base added equals the number of moles of acid originally present in the unknown. Solution concentration is typically reported in molarity (M), which is the number of moles of a chemical per liter of solution. The number of moles can be calculated from the solution concentration and the volume used:

$$\text{moles} = \text{molarity} \times \text{volume (in liters)}.$$

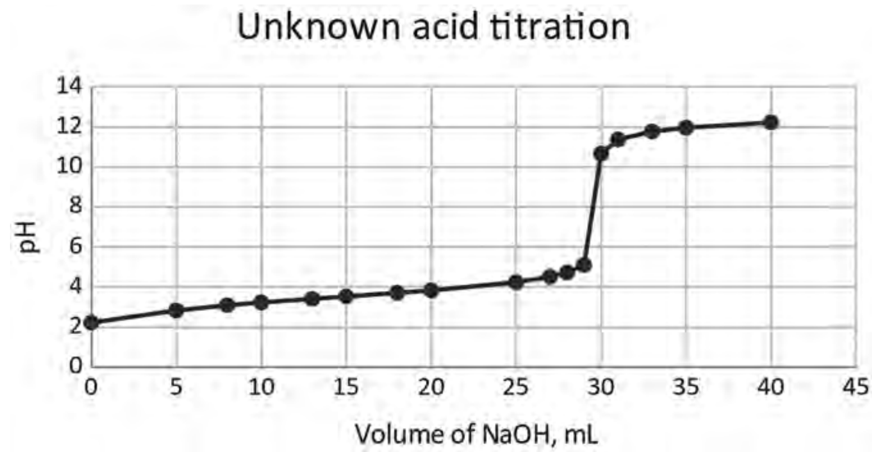
At the equivalence point in the reaction,

$$\text{moles of acid} = \text{moles of base}$$

or

$$M_{acid} \times V_{acid} = M_{base} \times V_{base}.$$

In a typical titration, the unknown acid is placed in a flask. A base of well-known concentration is placed in the buret. A pH meter is placed in the flask with the unknown acid. The pH is measured and plotted against the volume of base added to the acid. The result is an S-plot, as shown below.



The pH at the equivalence point can vary from the expected neutral 7.0 because of the hydrolysis of the salt, A^-, in water. The equivalence pH is best determined from the inflection point in the S-curve, which occurs in the near-vertical portion of the plot. By approximating the first derivative and looking for its maximum, the equivalence point can be calculated. When the equivalence point is known in terms of pH and volume of base, the concentration of the unknown acid can be calculated, as described above.

There is more information to be had from the titration curve! There is a second slight inflection point half-way to the equivalence point, in the nearly horizontal portion of the S-curve preceding the equivalence point. From this inflection point, the dissociation constant for a weak acid can be determined. Consider the equilibrium for a weak acid:

$$HA \rightleftharpoons H^+ + A^-.$$

The extent of this equilibrium is represented by the acid dissociation constant, K_a, given by

$$K_a = \frac{[H^+][A^-]}{[HA]},$$

where [X] denotes the concentration of the quantity X. This K_a is valuable information about relative acid strength. At halfway to the equivalence point in the titration, half of the weak acid HA has been reacted to form its salt, A^-, and half of the weak acid remains. This means

$$[HA] = [A^-]$$

at half-way to the equivalence point. It also means that at half-way to the equivalence point we have $K_a = [H^+]$, or, in terms of base-10 logarithms,

$$pK_a = -\log_{10} K_a = pH,$$

since, by definition, $pH = -\log_{10}[H^+]$.

3.14.4 Implementation Plan

Formal Learning Objectives

Mathematical: Identifying an inflection point from measured data, identifying that it corresponds to a point with largest derivative, estimating values of the 1st and 2nd derivative from the data.

Statistical: Using a spreadsheet: creating a scatter plot, creating a new column with average rates of change from the data, creating a column with approximations of the 2nd derivative, comparing and analyzing results from using 1st and 2nd derivative approximations.

Materials and Supplementary Documents Spreadsheet file `Titration.xlsx`; internet access for an instructor to play any short YouTube video on titration.

Time Required This module is designed to take about an hour, with students working in groups of 2 to 4. This should allow most students time to complete the module and be ready to turn it in.

Implementation Recommendations This module is done in a weekly calculus lab period where students apply in new situations the content they've been learning in class. No introduction is necessary, but it may be a good idea to show the class a video of the process of titration at the beginning (in the past we used `https://www.youtube.com/watch?v=g8jdCWC10vQ`). The students will analyze data in a spreadsheet program such as Excel or Google Sheets. If students don't have access to technology, the instructor could work through and display the spreadsheet steps at the appropriate times. Students get to apply derivatives in context, on an example from chemistry, one they perhaps experienced in an earlier class.

Alternative Solutions It is useful to connect the 3 different approaches to identifying the equivalence point: (1) identifying where the pH curve has largest slope; (2) identifying where the 1st derivative has the largest value; and (3) identifying where the 2nd derivative changes sign, or finding the inflection point.

Common Errors and Questions Students in our cohorts ask about how to correctly approximate the 1st derivative using the data, after which they usually have no problems with the 2nd derivative approximation. The last question, in which the students are going to identify the acid used in the titration, also elicits questions because it requires several steps and includes terminology from chemistry.

3.14.5 Additional Information

This lab reinforces students' working knowledge of 1st and 2nd derivatives and their meaning and applicability in the context of data. It provides additional exposure to working with spreadsheets which is one of the soft skills developed in the course. Finally, there is a discovery aspect at the end, when the acid used in the titration experiment is identified.

This module can easily be adapted down to even precalculus level by emphasizing average rates of change and focusing on the point/interval where the rate of change is at a maximum. With the same goal, it can also be used in a calculus course prior to introducing second derivatives and inflection points. Laterally, the module can be extended by providing data obtained from titrations with other acids and having groups of students work with different data sets. Although we haven't done so, one could also attempt to fit the data with various model functions (see, e.g., Eaker 2000) and use them to calculate the various derivatives and quantities of interest.

Finally, the inflection point half-way to the equivalence point could also be incorporated into the lab and a connection to the dissociation constant, K_a, could be made explicit for the interested students.

References

Eaker, C. W. (2000). Fitting and analyzing pH titration curves on a graphic calculator.*The Chemical Educator 5*(6) 329–334. `doi.org/10.1007/s00897000426a`

Titration

Module with Solutions

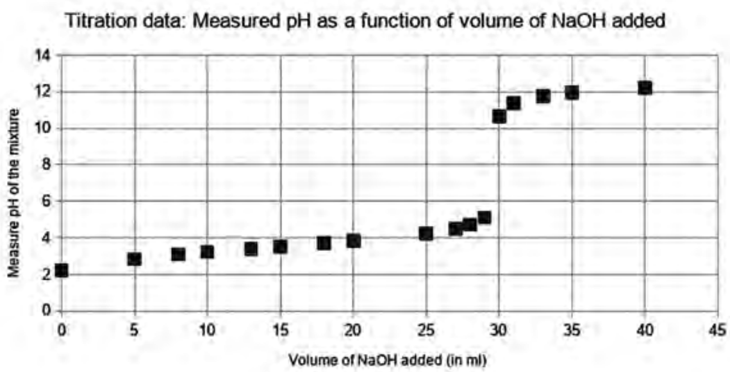
Titration is a method of chemical analysis in which a reactive substance is slowly added to another substance, and some property of the combined substance is measured. This procedure is typically taught in a General Chemistry course.

We will be looking at an example of acid-base titration. Specifically, 25 mL of an unknown monoprotic weak acid is titrated against 0.105M NaOH (which is a strong base). This means we are adding the base to the acid using a buret in a slow and precisely controlled manner. We measure the pH of the solution after each addition. (A solution with pH of less than 7 is acidic, and a solution with pH of more than 7 is a basic.) pH itself has no units.

1. Open the titration spreadsheet file. Explain in words what the point $(13, 3.41)$ means.

   Solution: This means that when 13 mL of NaOH are added to the acid, the pH is 3.41.

2. Create a scatter plot of the data. Do not connect the points. Sketch your plot below.



3. Imagine a smooth function $P(x)$ connecting the data points. What do the variables P and x represent, including units?

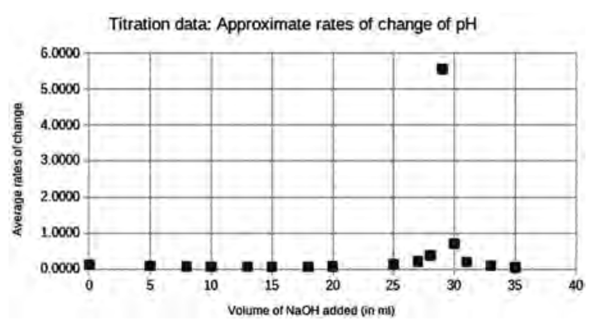
   Solution: P is the dependent variable, representing pH of the mixture (dimensionless, no units); x is the independent variable representing the volume of NaOH in milliliters.

4. How would you describe the function $P(x)$ in mathematical terms? (Consider terms like positive/negative, increasing/decreasing, concave up/concave down, maximum/minimum, etc.)

   Solution: On the shown interval, $P(x)$ is a positive function; it is increasing so doesn't have any local maxima or minima; it appears to change concavity twice: it starts off concave down, around $x = 15$ it changes to concave up, and then around $x = 30$ it changes to concave up again.

5. Write down a formula for the average rate of change of a function connecting points (x_1, y_1) and (x_2, y_2). Create a new column and calculate the rate of change between each pair of points. Put the first computed value into cell C4 and create a scatter plot of the computed values as a function of the values in column A. What observations can you make about your rate of change results? List a few things.

   Solution: AROC $= \dfrac{y_2 - y_1}{x_2 - x_1}$. All AROCs are positive. The values are initially quite small (below 0.1), then increase to the largest value of about 5.56, and decrease again below 0.1.



6. In titration we are interested in the *equivalence point*. **Chemically** this is when enough of the base has been added to completely neutralize the acid. **Mathematically** this is when the *rate of change is at its maximum*. How do we determine the equivalence point from P? How do we determine the equivalence point from P'? What does the data suggest? Estimate the equivalence point with these two approaches using your data and graph.

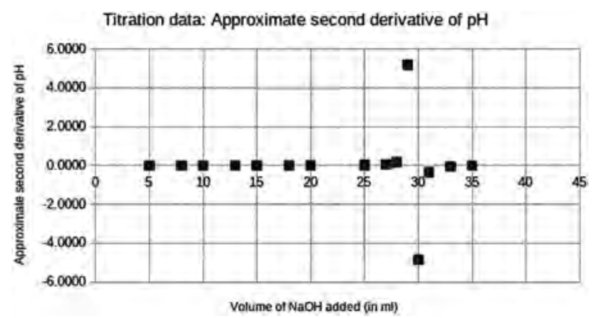
   Solution: Using P, we want to identify where it has the largest slope. Using P', we would be looking for its maximum. The data suggests this happens between $x = 29$ and $x = 30$ ml.

7. Suppose we have a formula for the titration function $P(x)$. What calculation would we want to do to find the equivalence point? What is our mathematical name for that type of point?

   Solution: To maximize $P'(x)$, we could solve the equation $P''(x) = 0$ for x and check that $P''(x)$ changes from positive to negative there. This is then an inflection point of $P(x)$.

8. Go back to your spreadsheet and calculate estimates of the second derivative. Put the first computed value into cell D5 and again create a scatter plot of the computed values. How many times does the second derivative change sign? What does that tell us about the concavity of $P(x)$? How would we determine the equivalence point from P''? What does the data suggest about the location of the equivalence point?

   Solution: The second derivative changes sign twice, starting off negative, then changing to positive, then to negative again. So, $P(x)$ changes from concave down to concave up to concave down. The equivalence point will be where the sign of the second derivative changes the second time. The data again suggests this is between $x = 29$ and $x = 30$ ml.



9. We are interested in when the second derivative is equal to zero. This actually happens a few times with our data set, but there is only one equivalence point. With our data there are a number of consecutive places early on where the second derivative is zero. To figure out why this happens, suppose we have a function whose second derivative is always zero. So we have $\dfrac{d^2y}{dx^2} = 0$. What is $\dfrac{dy}{dx}$ for this function?

   Solution: For such a function $\dfrac{dy}{dx} = c$, where c is any constant. That is, y has a constant slope.

10. What conclusion can be made from your observations in part 9.? Conclusion: If $f(x)$ is a ____________________ function on an interval, then $f''(x) =$ ______ on that interval.

    Solution: linear, 0

11. We are not interested in the places where the titration curve is linear, we are interested in where the concavity of the curve changes, specifically where it changes from concave up to concave down. Between what two data points does that happen? What is the concavity before and after the change?

    Between $x =$_______ and $x =$_______ the second derivative changes from ________ to ________.

    Solution: Between $x = 29$ and $x = 30$ the second derivative changes from *positive* to *negative*.

12. What is your best guess of the equivalence point for this titration? *(Your solution should be the mL of NaOH at the desired point.)*

    Solution: To provide a single solution, we can average the two x-values to get about 29.5 ml of NaOH.

13. The spreadsheet has a second page with more precise data near the equivalence point. Redo the scatter plot, and the first and second derivative calculations.

    Between $x =$_______ and $x =$_______ the second derivative changes from ________ to ________.

    What is your new estimate of the equivalence point?

Solution: Between $x = 29.7$ and $x = 29.75$ the second derivative changes from *positive* to *negative*. Averaging the two x-values, we get approximately 29.725 ml of NaOH.

Now solve for the value of K_a.

Solution: So, since the equivalence point is $x \approx 29.725$, half of that is 14.8625, and from our measured data the pH there is about 3.53 *(using $x = 15$ in the data)*.

Setting $3.53 = -\log_{10}(K_\mathrm{a})$, we obtain $K_\mathrm{a} = 10^{-3.53} \approx 2.95 \times 10^{-4}$.

14. Here's a list of common acids:

Acid	Use	K_a
benzoic acid	food preservative	6.5×10^{-5}
formic acid	ant bite sting	1.7×10^{-4}
acetylsalicylic acid	aspirin	3.0×10^{-4}
acetic acid	vinegar	1.8×10^{-5}
hydrofluoric acid	glass etching	7.1×10^{-4}

Which acid do you believe was used in our titration?

Solution: Based on our value $K_a \approx 2.95 \times 10^{-4}$, we conclude that the most likely acid was the acetylsalicylic acid (aspirin).