

Thermochemical Analysis of Neutralization Reactions: An Introductory Discovery Experiment

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This chemistry department has developed and implemented a set of experiments for our introductory curriculum called Discovery Chemistry (1–4). In this guided-inquiry method, a question is posed at the beginning of a pre-laboratory discussion that will lead the students to discover a chemical concept by laboratory experimentation. Student data are pooled and serve as the basis for post-laboratory class discussion and lecture.

In our first-semester general chemistry course, students discover the concept of stoichiometry by gravimetric analysis of six silver precipitation reactions, plotting product mass as a function of reactant mass (1). Subsequent lecture discussions use these data to discover the concepts of the mole, limiting reagents, and spectator ions. The interpretation of graphical representations of these data challenges our students to consider the meaning of stoichiometric relationships, treating them as more than word problems.

We elected to implement a new discovery experiment that uses thermochemical analysis to study neutralization reactions. This experiment reinforces our students' understanding of stoichiometry and allows for the discovery of basic concepts of thermochemistry before the introduction of the nature of the atom and bonding in our course sequence. We based this lab on an experiment examining the neutralization of citric acid previously described in this *Journal* (5) and used for many years at Harvard University (6). In this article, we discuss how we expanded this experiment to include a monoprotic and diprotic acid and modified it for our Discovery format.

Experimental Design and Results

Our Discovery Chemistry exercise begins with a pre-lab introduction to thermochemistry, acid–base reactions, and the concept of mole fractions. We then ask the students to predict the shape of a plot of the quantity of heat liberated by a neutralization reaction versus the mole fraction of base added. To aid the discussion, they are reminded of the data collected in our previous laboratory on the gravimetric analysis of the stoichiometry of precipitation reactions with silver salts (1). In that experiment, various quantities of silver nitrate are added to a constant quantity of one of a series of salts (e.g., sodium chloride), and the mass of the precipitate is plotted as a function of the quantity of silver nitrate added. Students provide various suggestions, including a directly proportional increase in heat or a shape similar to that obtained in the gravimetric analysis lab. We do not suggest which answer is correct, but leave that as our question to be discovered. We also ask them to consider what facet of the graph might change if the identity of the acid changed.

In the laboratory, students are divided into groups of four. They are assigned volumes of 0.800 M sodium hydroxide and 0.800 M solutions of lactic acid, oxalic acid, or cit-

ric acid, such that the total reaction volume remains constant at 50.0 mL. Within each group, one pair of students is assigned four sets of volumes that correspond to a mole fraction of base in the solution of 0.10, 0.30, 0.70, and 0.90, and the other pair of students is assigned the volumes that correspond to mole fractions of 0.20, 0.40, 0.60, and 0.80. The groups obtain about 125 mL of their assigned acid and an equivalent volume of sodium hydroxide. The acid and base are added to burets that have been labeled and rinsed. Using the burets, the assigned volumes for the first trial are dispensed into separate Styrofoam cups, and the temperature of each is measured with a digital thermometer. The contents of one cup are then added to the other and mixed by swirling. Once a stable temperature is reached, it is recorded. The solution is saved in a waste beaker, the cups are rinsed and dried, and the remaining three trials are completed in a similar fashion.

The students calculate the heat liberated, q , for each trial using the formula

$$-q_{\text{rxn}} = q_{\text{water}} = mc\Delta T$$

The mass of solution, m , is calculated by assuming the solutions have the same density as water, and the specific heat, c , of the solution is assumed to be the same as that of water. The difference in temperature, ΔT , is that between the final temperature of the mixture and a weighted average of the initial temperatures in the two cups before mixing. Students are instructed to calculate the mole fractions for each of their sets of volumes and to use the pooled data of their group to plot the absolute value of the heat of neutralization in Joules versus the mole fraction of base added. They are instructed not to attempt any “best-fit” analysis.

In the post-lab discussion, a transparency is made of a student data set for lactic acid and presented to the class. Students are asked to make observations about the data set and how it compares to what was expected in the pre-lab. They are also asked to suggest a manner in which a “best-fit” line may be fit to the data, and students will usually suggest that two separate lines be drawn. This is a good place to discuss the appropriate use of the y intercept as a data point at mole fractions of zero and one. At this point, the instructor suggests that the lines might be extrapolated. The extrapolated lines cross at a mole fraction of 0.50 for this example, and students are asked if they can draw any conclusions about the stoichiometry of the reaction from this fact. From the conclusion of 1:1 stoichiometry, a balanced equation is written to describe the neutralization reaction. Students are then asked what they would expect the graph to look like if the acid were diprotic. They usually predict that the mole fraction at the apex should change, although some sections require guidance to the value of 0.67 by the instructor writing the definition of mole fraction on the board. Students also often predict a doubling of the heat liberated at the apex. They are then shown the plot for oxalic acid. First, the mole

fraction value is discussed, and a prediction is made for a triprotic acid and confirmed with the plot for citric acid. This is followed by writing balanced equations for each neutralization reaction. We then discuss which reagent is limiting for each part of the curve and discuss the incorrect prediction that the heat liberated at the apex should double for oxalic acid and triple for citric acid. Students are then required to calculate the average heat of neutralization per mole of acid for each of their data points and report the average value as part of their conclusion in their notebook, to be graded the following week. Student data are presented in Figure 1 for the neutralization of lactic, oxalic, and citric acids.

For the sample student data, the average heat of neutralization of lactic acid was -56 kJ/mol, that of oxalic acid -104 kJ/mol, and that of citric acid -157 kJ/mol. The mole fractions at the apex are approximately 0.5, 0.67, and 0.75, as expected. Our data are not sufficiently precise to account for any variation near the apex or to discern the contribution of the heat of dissociation of the weakly acidic protons to the measured heat of neutralization. However, as observed by Hayes, the differences between the heats of dissociation of the three acidic protons of citric acid are small relative to the heat of neutralization (5, 7). Literature values for the sum of the heats of dissociation in water are 2.92 kJ/mol for citric acid (8), 3.1 kJ/mol for oxalic acid (8), and between -0.68 and -0.78 kJ/mol for lactic acid (7). This experiment nicely sets the stage for a lab in our second-term general chemistry course. In that experiment, students discover the contribution of the heats of dissociation of sulfuric acid or bicarbonate to the overall heat of the neutralization reactions with sodium hydroxide and compare these results to those obtained by the neutralization of two strong acids (1).

Hazards

Solutions of citric acid, lactic acid, oxalic acid, and sodium hydroxide are all corrosive and irritants, and oxalic acid is toxic. Goggles, gloves, and appropriate lab attire should be worn at all times, and all solutions used in this lab should be disposed of as hazardous waste according to official procedures.

Discussion

This lab has been very useful in reinforcing the discovery of the limiting reagent. In our previous gravimetric analysis lab, students plot the quantity of solid product formed versus the quantity silver nitrate added to a constant quantity of chloride, bromide, or oxalate salt (1). They accept that this plot should rise with a slope dependent on the stoichiometry, form a cusp once both reagents are consumed, and that further additions of silver nitrate will not increase the quantity of product formed. However, the results of this thermochemical analysis challenge their understanding of limiting reagents, and they initially struggle to explain why the slope should be negative after the apex and not level off as in the previous experiment. Although they can identify that the base is limiting to the left of the apex, they initially have difficulty explaining why the acid should be limiting to the right of the apex. In a followup lab assignment turned in for credit, we ask the students to calculate the average enthalpy of neutralization for their acid, which requires them to understand the relationship between the heat liberated at each point and the moles of the limiting reagent at those points.

In the first year we introduced this lab in our course sequence, we assigned students mole fractions and required that they determine the appropriate quantity of acid and base to add to reach that mole fraction. We abandoned this approach for two reasons. First, if a group makes an error in their calculations, their partner group that depends on that contribution to the pooled data is at a disadvantage. At this point in the course, we find that some students struggle with this calculation. Second, we find that performing the calculation of mole fraction from the volume data helped the students to be able to predict the mole fractions at the apices of the plots and minimized anticipation of the result that would interfere with the discovery process.

The addition of lactic and oxalic acids contributes to the discovery aspect of the lab. The discussion in the post-lab period is started by consideration of the monoprotic lactic acid, which allows the students to make predictions about how the plots for other acids should differ. In some cases, students discover that their predictions are not correct. We

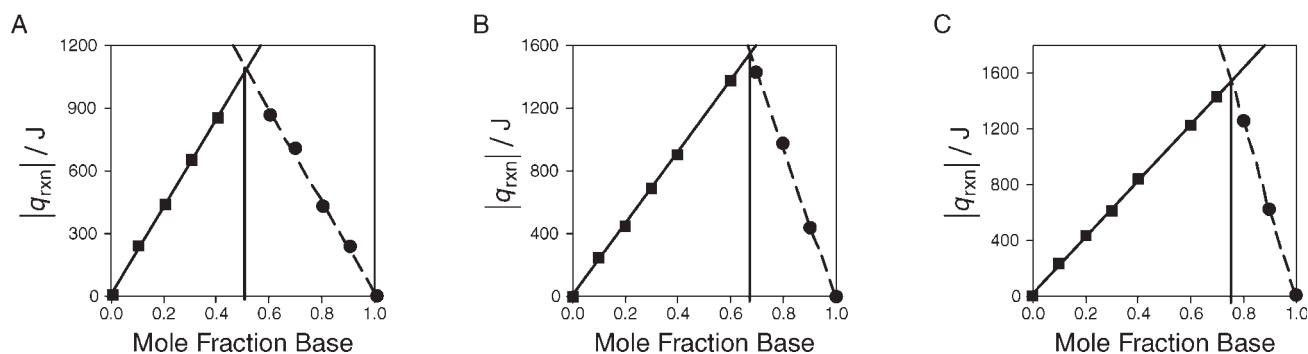


Figure 1. Representative student data for neutralization of (A) lactic acid, (B) oxalic acid, and (C) citric acid. Data to the left and right of the apex were separately fit by a linear least-squares analysis using KaleidaGraph (Synergy software).

find that this guided-inquiry method aids understanding and retention. For instance, when we only used citric acid, students appeared to memorize that the moles of acid neutralized to the left of the apex was the moles of base divided by three. However, considering all three plots forces them to relate this calculation to the stoichiometry of the balanced equation.

This lab requires about a 60-minute pre-lab session with the instructor, a 15-minute session with the lab coordinator to reinforce the proper use of the glassware, about 2 hours for data collection and pooling, and about 45 minutes of post-lab discussion, followed up in the classroom lecture period. If acid–base chemistry has been introduced previously in the course, the pre-laboratory session may be shortened.

Acknowledgments

The authors thank Rick Herrick of Holy Cross for useful discussions and suggestions, Gregg Tucci, Jim Davis, and Logan McCarty of Harvard University for useful discussions and for introducing us to this lab and to the Holy Cross faculty who have run this lab in their courses. This material is based upon work supported by the National Science Foundation under CAREER grant No. 0447647.

Supplemental Material

Instructions for the students including a data sheet, notes for the instructor, teaching assistant guidelines, and followup exercise are available in this issue of *JCE Online*.

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