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Aqueous Equilibria: Acids, Bases, and Solubility. A General Chemistry Laboratory Experiment

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Abstract: We refer to two major types of general chemistry freshman laboratory experiments: discovery and cookbook. The typical Freshman enrolled in general chemistry has the skills to perform an experiment that is somewhere between cookbook and discovery, and we have developed a laboratory experiment that is midway between these extremes. This experiment aids the student's understanding of the concept of aqueous equilibria. In this experiment, students are asked to prepare and measure the pH of a variety of acidic and basic solutions. Students are also asked to calculate pH values from literature dissociation constants and dissociation constants from their experimental pH values. This experiment demonstrates the relationships between dissociation constants, percent ionization, pH and strength of acids and bases, as well as molar solubility and the solubility product constant, K_{sp}. A Mathcad-based prelaboratory activity provides a review of the concepts and engages students in what-if explorations.

Introduction

No one disputes the value of laboratory experience in helping students understand the concepts presented in lecture; however, laboratory activities should also aim to enhance student's thinking and problem-solving skills. Most traditional experiments are cookbook experiments that require no previous laboratory experience. These experiments test how well a student can read and follow directions without utilizing any critical-thinking skills. Discovery laboratories are the opposite; they require the student to have some previous laboratory skills and an understanding of various laboratory techniques.

The skill of a typical Nicholls State University general chemistry student is somewhere between no laboratory experience and two years of high school laboratory experience. To accommodate the variety of students found together in our laboratory course, we have developed an experiment, which we term *guided discovery* that eliminates the detailed cookbook directions while helping to develop the critical-thinking skills of the student.

Aqueous equilibria concepts are covered in one experiment with the students exploring strong and weak acids or bases in terms of pH, dissociation constants, and solubility limits on the use of calcium hydroxide as a strong base.

The experiment is preceded by computer activities using Mathcad. Calculations involving pH, [H †], K_a , K_b , and K_{sp} are all performed by the students before the experiment, to review concepts taught in the lecture course and to determine the expected experimental results for a fictitious system. After the experiment, the fictitious values are replaced by experimental values and the students examine the relationship between their value of the dissociation constant and the literature values.

We introduce the guided-discovery type of experiment after the students have completed several typical cookbook-type experiments. We want to make sure all of our students are on the same level regarding basic laboratory safety, procedures, and techniques. During this time, we also work on enhancing their writing skills. After preliminary cookbook experiments are completed, the students are comfortable, both in the laboratory and working with computers; this enables the students to better evaluate their experimental results.

The main difference between a guided-discovery experiment and a discovery laboratory is that in guided-discovery experiments questions are presented in such a way that students are forced to constantly interpret results and verify concepts. In this experiment on aqueous equilibrium, our guided discovery is implemented in the actual investigation of what is meant by the terms strong or weak for acids and bases and the relationship between percent ionization and strength. Students typically memorize the list of strong acids and bases without really understanding the meaning, frequently confusing the terms strong and weak with concentration. In this experiment students are asked to prepare and measure the pH of a variety of acidic or basic solutions and determine which acids and bases are strong or weak. Students compare pH values based upon literature values for dissociation constants with the calculated dissociation constants from their experimental values. Students are asked to suggest reasons for any differences. The students also use pH measurements to determine the solubility and $K_{\rm sp}$ of Ca(OH)₂. Calcium hydroxide is a strong base, but due to the limits of solubility, attempts to prepare solutions with concentrations greater than 0.021 M, yields solutions with the same pH (as the saturated solution). While this is mentioned to the student in the lecture, they do not fully comprehend this phenomenon until they see it for themselves. By having the students prepare a solution greater than 0.021 M (0.050 and 0.10 M), the fact that some solute remains undissolved aids in their understanding of the concept of molar solubility. Another advantage of a guideddiscovery experiment is that any instructor or teaching assistant can utilize it without modification. Directions are detailed enough that students can figure out what to do, although they must still think about what they are doing. Typical discovery laboratories tend to be difficult for some instructors or teaching assistants to direct without students missing the major concepts expected to be learned. Guided discovery is an alternative for the student, allowing them to perceive experiments as something other than just a rehashing of old material.

Both the student and the instructor monitor the results throughout the experiment. Students are instructed to repeat solution dilution when the pH varies by more than 0.1 pH units. This constant feedback reinforces both the understanding of the concept and the development of laboratory skills. By comparing the experimental and theoretical results, the students are able to analyze their own skills and techniques and see the necessity of care in preparing solutions. It also gives the student the opportunity to analyze results and to speculate reasons for any deviation.

In the typical lecture course, the general chemistry student should have covered the various concepts of equilibrium and equilibrium constants. An experiment such as this allows for various concepts, such as acid dissociation (K_a) , base dissociation (K_b) , and solubility product (K_{sp}) , to be investigated at the same time so the students can see their relationships. In the pre- and post-laboratory activities, the student reviews the concepts of equilibrium and the mathematical calculations for pH. To aid the students in calculating and connecting the relationship among pH, [H'], and K_a/K_b, Mathcad activities are assigned before the experiment is performed. Mathcad is introduced early in the semester and is routinely used for data analysis prior to this experiment. By the time they encounter this experiment on aqueous equilibrium, students are quite proficient in using Mathcad (see supporting materials). The Mathcad component has the advantage of making the students think about the relationships among the concepts of aqueous equilibria. Students must do more than just "plug and chug." They are engaged in the process of translating ideas into mathematical equations. Exploring what will happen with the numerical values under different scenarios enhances understanding of the

A similar exercise is presented using the molar solubility of calcium hydroxide. Post-laboratory calculations are facilitated because the pre-laboratory Mathcad documents are simply modified by replacing the fictitious values with experimental data. This allows for additional discussions after the experiment of the chemistry involved.

For most experiments in a general chemistry laboratory, the solutions of the appropriate concentration are prepared prior to laboratory class. In the interest of saving time and consistency of the experiments, the actual processes of preparing solutions or making serial dilutions is not usually covered in general chemistry laboratory. Although this seems like a trivial technique, it is crucial that students understand how solutions are prepared. Solution preparation is a very real skill that all chemistry students need to learn. We feel students need the experience of making solutions, connecting the lecture calculations to the laboratory. We stress in lecture the details of concentration, and the students are given homework and examination questions as to how much solute is needed to prepare a solution of certain concentration. Unfortunately, the typical student cannot translate this knowledge to the laboratory, and most general chemistry experiments do not require them to do so. In this experiment, we require the students to calculate the quantity of substance needed to make a solution and require them to prepare the solutions. Our handout does not provide very detailed procedures so that students are forced to make decisions regarding solution preparation. For example, the second step of the procedure simply instructs them to "prepare 100 mL of 0.0100 M solution for four reagents using 0.10 M stock solution." (See the supporting material for the complete experimental procedure). Students struggle at first with the vague procedures but adapt quickly.

The concentrations of the solutions were chosen so that final results will not deviate much from ideal results and trends; however, there is some deviation from the literature value in the $K_{\rm sp}$ for calcium hydroxide because the ionic strength and temperature are not reported at 25°C. Although the deviation occurs, the result still demonstrates to the students the limits of solubility for calcium hydroxide and that solutions of 0.050 and 0.10 M are not truly obtained.

As with all experiments covered in general chemistry laboratory, having the students complete a laboratory report enhances writing skills. The procedure and observation section becomes more significant to them because they cannot simply go back to the laboratory handout and summarize information or look up numbers. The importance of diligent notebook work is emphasized.

The complete experimental procedure and typical student results can be found in the supporting material. Instructor comments are also available.

Experimental

No major instrumentation is required for this experiment and the required chemicals and supplies are usually available in most general chemistry laboratories. The equipment required is a hot plate, balance, 1000-mL beaker, a 500-mL Erlenmeyer flask with stopper (#7), three 250-mL Erlenmeyer flasks with stoppers (#6), a 1.00-mL transfer pipette, four 100-mL volumetric flasks, a fimnel, filter paper, and pH meter (four-pocket meters will suffice). The chemicals required are deionized water, 2.0 g of Ca(OH)₂, and 2 mL each of 0.10 M stock solutions of HCl, HC₂H₃O₂, NH₃, and NaOH.

This experiment can be easily completed in a typical three-hour laboratory session. If desired, and with time permitting, the experiment can be carried out over two laboratory sessions to allow class time for discussion of the results and to use the computers for the Mathcad activities. Generally, we try to have the second laboratory session for student feedback and to confirm that they understand the results.

In the laboratory, the students first prepare three 100-mL solutions of calcium hydroxide with concentrations of 0.0050 M, 0.050 M, and 0.10 M using freshly boiled and cooled deionized water. After allowing the solutions to settle, the calcium hydroxide solutions are filtered and the pH of the filtrate is measured using a calibrated pH meter.

Students then dilute the four aqueous stock solutions (0.10 M) using pipettes and volumetric flasks to prepare 0.0010 M solutions. Next, the pH is measured for each of these solutions. If the pH varies by \pm 0.1 pH units, the students are instructed to either measure pH again or prepare a fresh solution. Questions are presented in the handout for almost every step to encourage the students to think about what they are doing and why each step is necessary. Once the experiment is complete, dissociation constants are calculated and the results compared to the literature values.

Conclusion

With this guided-discovery experiment we have found a way to enhance students' thinking and problem-solving skills by bridging the gap between cookbook experiments, which require little to no critical thinking by the student, and discovery laboratories, which are a bit beyond our first-year students' abilities in a first-semester laboratory course. This experiment also covers important concepts of aqueous equilibria in general chemistry.

With previous experiments we found that the students have difficulty understanding the concepts associated with aqueous equilibria; this experiment is extremely useful in advancing that understanding and in clarifying misconceptions. Some of the results deviate slightly from those expected by literature values, mostly because of differences in ambient temperature and student error. Still, all the trends are followed, as expected, helping students to obtain a better grasp of the subject matter. Most students feel that this experiment helped them comprehend aqueous equilibria and complemented lecture material. Instructors who teach the related lecture course see an improvement in their student's understanding of the material. The typical student shows improvement in

performance in their next chemistry course, quantitative analysis, which covers aqueous equilibria in great detail. The student response is favorable for this type of experiment and the results of subsequent lecture examinations lead us to believe that the students have a better understanding of the concepts used in this experiment.

The guided-discovery format is extremely helpful to students. The many questions asked of them throughout the procedure keep them thinking about why they are performing the steps and they are constantly reminded of the connection of lecture material to the laboratory. The added feature of Mathcad activities reinforces the relationships explored in the experiment.

Supporting Material. Mathcad samples are available at *The Chemical Educator's* website (http://dx.doi.org/10.1007/s00897000433b) or the author's website (http://chem.nich.edu/mathcad). A student handout is available at http://dx.doi.org/10.1007/s00897000433c