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The Determination of the Dissociation Constant of a Weak Acid by Titration: An APCELL Experiment.*

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Acid/base systems are of fundamental importance in many areas of chemistry, biochemistry, environmental science and biology but receive little attention after the traditional general chemistry course in first year. In recent years there has been a questioning of the validity of the equilibrium calculations usually carried out in these courses but few of the standard texts used in such courses make any attempt to point this out. In the absence of a rigorous thermodynamic treatment of aqueous systems, students are unaware that in real systems equilibrium constants have a strong dependence on the ionic strength of the solution. As most tables of equilibrium constants in aqueous systems refer to the thermodynamic equilibrium constant at infinite dilution the use of these values in dilute ionic solution can lead to considerable error.

This experiment was designed to reinforce the basics of acid/base chemistry through the determination of the dissociation constant of a weak acid in the presence of an inert electrolyte. Experimentally the experiment is straight forward but allows the student to carry out optional extensions including the potential for observing the effect of varying values of K_a and K_w on the shape of the titration curve.

Even though the data collection process is a bit tedious it does give the student a good set of data on which to base their calculations. I believe the challenge in physical chemistry is always to develop an experimental method that will give the experimenter reliable and reproducible data, then the subsequent collection of that data will become somewhat less challenging.

The experiment exposes the student to the possibility of manipulating the data in several ways, arriving at a conclusion about which method may be the most appropriate and to think about the assumptions involved in each of the treatments. A comparison between the determined value of K_a and the literature value will show a significant difference.

* The complete documentation for this experiment is freely available on the APCELL web site [www.apcell.org]. This includes the educational template, a set of student notes, demonstrator notes and technical notes to allow ready implementation into a new laboratory.

The student is able to explore the power of a spreadsheet package such as Excel for the handling of large data sets. The extension introduced allows students to do some simple mathematical modelling of the titration curve and to use K_a and K_w as adjustable parameters to obtain the best fit between calculated and experimental data. Although the goodness of fit is obtained visually, it does introduce the student to the concepts involved in more rigorous calculations.

Educational Template

Section 1 – Summary of the Experiment

1.1 Experiment Title:

The Determination of the Dissociation Constant of a Weak Acid by Titration

1.2 Description of the Experiment

The acid strength of a weak acid as measured by the dissociation constant, K_a, is of relevance in many areas of chemistry and in biological systems. Weak acids are an integral component of buffer systems and the range of a buffer is controlled by its pK_a. In this experiment students can build on these basic skills by

- following the progress of a titration potentiometrically
- see how the pH changes during the titration use the pH-volume data to estimate the equivalence point by different methods
- determining the dissociation constant of the acid by several techniques including the Gran technique which is not normally covered in a physical chemistry course.

By carrying out the titration at constant ionic strength, students can also see that the value of K_a is significantly different from the thermodynamic K_a usually reported in the literature.

The calculations involved are not complex and can readily be carried out using a spreadsheet. Depending on the time available the titration can be modelled using a spreadsheet to carry out the calculations either as an integral part of the experiment or as an extension. This enables the student to explore the effect of changing the value of K_a, on the fit of the calculated results to the experimental pH/Volume curve.

1.3 Course Context and Students' Required Knowledge and Skills

The basic theoretical skills (weak acids and bases, pK_a, pK_b, pK_w, buffers, etc) are covered in the typical textbook of General Chemistry used in first year courses. First year chemistry courses cover the basic skills of titration and in some cases students would use a pH meter to measure pH and so be familiar with its operation. The mathematical skills required are algebraic and should not be beyond the average student.

Acid strength is an important concept in most areas of chemistry but its formal study after first year would normally be limited to analytical chemistry courses. This experiment provides a reinforcement and extension of first year concepts in this area.

1.4 Time Required to Complete:

Prior to Lab	1 hr
In Laboratory	3 - 6 hrs
After Laboratory	1 - 3 hrs

1.5 Acknowledgments

The original experiment was based on a description of the determination of stability constants.[1] The theoretical treatment for the simulation of the titration was initially taken from Harris.[2] A more recent treatment with relevance to the spreadsheet approach is in the Fifth Edition of the same text, p294.

1.6 Any Other Comments:

The experiment is open-ended. Students can repeat the experiment at different ionic strengths, use the same approach on a diprotic acid or look at the effect of substitution on acid strength.

Section 2 – Educational Analysis

Learning Outcome *What will students learn ?*	**Process** *How will students learn it?*	**Assessment** *How will staff know students have learnt it?* *How will students know they have learnt it?*

Theoretical and Conceptual Knowledge

K_a is a function of ionic strength.	By comparing the experimental value at a known ionic strength with the literature value at zero ionic strength.	By the student commenting on the difference between the two values in their laboratory report. By realising the difference between the experimental and the literature values are significant.
Practical application of weak acid/base theory.	By calculating the value of K_a by several methods from different applications of the same basic equation to their experimental data.	By the students demonstrating that they can carry out the relevant calculations and being able to critically compare the values of K_a, by the different methods. By being able to understand the derivation of the relevant equations.
The application of computer modelling to simulate experimental results.	By rearranging the master equation for the titration into a suitable form for spreadsheet analysis and carrying out the analysis.	By the presentation of the calculated and experimental titration curve in the laboratory report. By being able to produce a titration curve that approximately matches the one obtained experimentally.
Be able to solve acid base problems.	By being able to understand the derivations being presented and to derive an equivalent equation for the titration of a weak base with a strong acid.	By deriving the relevant equations.

Scientific and Practical Skills

To be able to critically evaluate the 'best' method for determining the equivalence point of a potentiometric titration.	By recognising the error involved with determining the volume at the point of inflexion on the titration curve.	From the discussion by the student in the laboratory report. By determining the equivalence points by the methods described in the experiment.
To be able to critically evaluate the'best' method for determining the value of K_a.	By evaluating the uncertainty in the determined values.	From the error analysis undertaken by the student. By being able to carry out an error analysis on the results.
To be able to calibrate a pH meter using appropriate buffers.	By carrying out the calibration after being instructed by a demonstrator.	The pH values recorded during the titration are what would be expected. By obtaining a K_a value in reasonable accord with the literature.
To be able to use a spreadsheet to present a large amount of data in an appropriate graphical form.	By being instructed in the basic principles of using spreadsheet (if required) and how to apply it to the data from this experiment.	From the presentation of the appropriate plots in the laboratory report. By being able to produce suitable plots for the laboratory report and to obtain the required K_a and equivalence point from the plots.

Generic Skills

Manipulation of complex algebraic equations into a suitable form for analysis.	By rearranging the equations given into a suitable form for plotting.	By producing appropriate plots of the measured data. By determining the equivalence points by the methods described in the experiment.
Carrying out appropriate error analysis on the experimental results.	By estimating the uncertainties in the various experimental values obtained. Carrying out a least squares analysis on the Gran plot to estimate the standard deviation in the value of K and the equivalence point.	From the error analysis undertaken by the student. By being able to carry out an error analysis on the results.

Section 3 – Student Learning Experience

3.1 Did this experiment help you to understand the theory and concepts of the topic? If so, how, or if not, why not?

S1: Yes it helped me consolidate theory.

S2: The experiment allowed me to understand the importance of using several methods in interpreting experimental data. It also reinforced the ideas of accuracy in standardisation and titration.

S3: Yes, the difference between the true thermodynamic equilibrium constant and the concentration equilibrium constant. However for general theory on K_a, it wasn't very helpful at all, as what we were doing was determining one dissociation constant.

3.2 How is this experiment relevant to you in terms of your interests and goals ?

S1: This experiment was relevant to consolidate theory from lectures.

S2: I enjoy titrations and standardising acids and bases. It was relevant in that it helped me to gain a better understanding of these methods and it also introduced me to the use of the glass electrode - which I hadn't used before.

S3: In so far as "interests" and "goals" referring to my personal understanding of the material, the experiment wasn't all that relevant.

3.3 Did you rind this experiment interesting? If so, what aspects of this experiment did you find of interesting? If not, why not?

S1: I found the results interesting.

S2: Although the actual method was repetitive, I found the analysis of the experimental data quite interesting. This was largely due to the fact that I had a reasonable understanding of what I was doing and why.

S3: No. Nothing was demonstrated about how K_a varies with strength of acid. We only found K_a for a weak acid.

3.4 Can the experiment be completed comfortably in the allocated time? Is there time to reflect on the tasks while performing them?

S1: The experiment can be completed comfortably in the allocated time. There is some time to reflect on the tasks.

S2: I easily completed the experiment in the allocated time. Although I had to restandardise the CH_3COOH, I still finished completely in one week (4 hr). I found this very beneficial as it allowed adequate time to reflect on and interpret results.

S3: Yes to both questions.

3.5 Does this experiment require teamwork and if so, in what way? Was this aspect of the experiment beneficial?

S1: The computer work required some assistance which was beneficial.

S2: The experiment can be successfully completed individually. Standardised solutions could be shared but for accurate results etc I wouldn't advise it. Plus the experiment can be easily completed individually within the allocated time.

S3: No.

3.6 Did you have the opportunity to take responsibility for your own learning, and to be active as learners?

S1: Yes.

S2: Opportunity to take responsibility for my own learning during this prac really only came into play in looking up the literature values and looking in other texts for explanations about the Gran method and pH-volume curves etc. However this kind of responsibility was applicable in all experiments.

S3: Yes. These pracs are good for you to take responsibility for your own learning. If you don't understand, you have to ask and if you don't ask you went anywhere.

3.7 Does this experiment provide for the possibility of a range of student abilities and interests? If so, how?

S1: Yes. It involved using Excel, making graphs and using different equipment

S2: I believe that this experiment adequately provides for a range of abilities. This is largely due to the fact that the 'hard parts', such as the standardisation and titration, are really the basis of the majority of chemistry experiments. Also there was a variety of ways to analyse the data hopefully allowing students to at least understand a couple of ways.

S3: No not really.

3.8 Did the laboratory notes, demonstrators' guidance and any other resources help you in learning from this experiment? If so, how?

S1: Yes. It provided clear instructions on the experiment and theory.

S2: I found the demonstrators to always be very helpful in aiding my understanding of the various components of the different experiments. I also found the different approaches to some topics in various texts to be helpful, as there usually was at least one way that I understood!!

S3: A little, in the introduction but not much.

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S1: Good because I leant how to make different graphs and it linked experiment to theory.

S2: I found the experiment both enjoyable and reasonably easy to understand and conduct. I found the procedure to be clearly written and easily followed. (It was definitely one of my easier experiments - both in procedures and in the write up).

S3: Computer work OK. Could draw clear graphs

3.10 What improvements could be made to this experiment?

S2: I don't have any suggestions of improvements as such. The only thing I would suggest would be that an alternative measure of the pK_a could be included (if one exists) that uses a different procedure so that new skills could be acquired.

S3: Explanation in introduction of how K_a, changes with acid strength (even though I know this is first year material) and maybe compare K_a of different acids or find K_a of a range of acids.

3.11 Any Other Comments

S2: I found the experiment both enjoyable and fairly easy to understand, perform and write up. It helped me confirm my ideas about standardisation and titration. Although it was a good prac (because it was short - no just kidding) I thought that the actual procedure taught me nothing new. I mean no new methods were introduced and used during the actual experiment itself. The write up used various different techniques of analysis which I found very useful and beneficial to my overall understanding of the prac. Overall I would say that the prac was well written, easy to follow, good to perform and relatively easy to write up.

S3: Also explanation of theory for point of inflexion, pH-volume curve, Gran plot etc.

References

1. A. E. Martell and R. J. Motekaitis, *The Determination and Use of Stability Constants.* 2nd Edition, VCH Publishers., (1992).

2. D. C. Harris, *Quantitative Chemical Analysis,* 2nd Edition Freeman and Co., New York, (1987), 253-254.