

# Determination of Thermodynamic Values ( $\Delta S^\circ$ , $\Delta H^\circ$ , and $\Delta G^\circ$ ) from the Dissociation of a Weak Acid

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**Abstract** The concepts of equilibrium and thermodynamics are among the most important topics covered in a general chemistry course. The thermodynamic properties  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are difficult to measure directly in a laboratory setting, but can be determined by monitoring the temperature dependence of the equilibrium constant,  $K$ . Previously published procedures require sophisticated technology or methodology, such as simultaneously measuring temperature and absorbance using a spectrophotometer, which may be unavailable to small and/or rural colleges and universities. Measuring the pH of a weak acid solution while varying the temperature allows for this analysis to be conducted simply, making it more accessible to broader range of academic laboratories. This experiment outlines the simple measurement of the equilibrium constant and temperature, with aspects of graphical analysis, allowing students to link the concepts of equilibrium and thermodynamics conceptually and mathematically. Calculated values of  $\Delta G^\circ_{298}$  are consistent with literature values, indicating that the experiment is suitably robust to be performed successfully by students of a wide range of skill levels.

**Keywords:** first-year undergraduate/general, laboratory instruction, hands-on learning, equilibrium, thermodynamics

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## 1. Introduction

The concepts of equilibrium, thermodynamics, and the connection between the two are cornerstone concepts covered in a typical general chemistry curriculum. [1] A well-known fundamental equation relates the Gibbs free energy ( $\Delta G^\circ$ ) and equilibrium constant ( $K$ ) via the gas constant ( $R$ ) and the absolute temperature ( $T$ ): [2,3,4]

$$\Delta G^\circ = -RT \ln K. \quad (1)$$

The  $\Delta G^\circ$  itself can be calculated from two other properties, enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ), which are related through the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (2)$$

Equations (1) and (2) can be combined to give the van't Hoff equation:

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (3)$$

This relationship allows the determination of thermodynamic quantities from the value of the equilibrium constant over a range of temperatures.

Laboratory investigations of this linkage with different parameters have been published using a variety of techniques such as titration, flame emission spectroscopy, emission & absorption spectroscopy, and calorimetry. [5-13] However,

many of these analyses require instrumentation that may not be widely available to all laboratories, or require more sophisticated procedures that are unsuitable for an introductory audience. In the interest of bringing this concept to a broader group of students, an alternate methodology was developed to perform the analysis based on just the natural dissociation of the acid as determined by pH and temperature measurement. The procedure and material requirements are light enough to allow this experiment to be performed in high schools (AP Chemistry curricula) or at colleges/universities where resources are limited.

The experiment was developed and implemented to answer the following research question: Can the incorporation of this activity improve student success rates on typical calculations presented as part of summative assessments at the conclusion of a second semester course in General Chemistry, specifically acid-base equilibrium calculations?

## 2. Materials & Methods

The analyte, 1 M acetic acid, was prepared by dilution of glacial acetic acid. Sodium hydroxide solutions of equal concentration were provided to students to neutralize the acetic acid solutions so the spent solutions could be disposed of safely down the drains in accordance with local environmental regulations. pH buffers (4 and 7) were used to calibrate pH probes. Ice from a laboratory ice machine was used to cool the samples.

## 2.1. Educational Research Method

The experiment was developed and implemented as part of a second-semester STEM majors General Chemistry course at a public university in rural Tennessee. The course has multiple lecture sections with approximately 100 students each, with different lecturers for the individual sections. The laboratory is broken into sections of a maximum of 60 students each and are not aligned with a specific lecture section, with the individual lab sections under the direction of a faculty instructor or graduate teaching assistant. The experiment was implemented concurrently with the curricular change from a classical approach with one textbook and homework system to an atoms-first approach which used a different textbook and homework system.

Student data was evaluated during the second semester portion of the course in three academic years (Y1, Y2, and Y3). The baseline data was acquired during the last semester of the standard approach (Y1); the last two years (Y2 and Y3) were based on students taking the atoms-first curriculum. The changes in the atoms-first curriculum are much more significant in the first half of the General Chemistry course, though it should be noted that in the atoms-first textbook used, the thermodynamics chapter precedes the discussion on equilibrium, whereas in the standard approach, equilibrium was covered prior to thermodynamics.

To assess the impact of the experiment, student success rates (percentage of correct responses) were monitored for two particular questions on an ACS full-term standard exam administered as a final exam in the second semester General Chemistry course. The questions were selected based on the similarity of the content tested relative to the content of the experiment.

Student attitudes toward the experiment were gauged using an end-of-semester evaluation, delivered to all students in the laboratory curriculum through the learning management system (LMS), for which a small amount of bonus credit (0.25% of the lecture course grade) was offered for completing the survey. The evaluation covered the entirety of the laboratory curriculum and probed student's impression of the overall laboratory experience, as well as attitudes toward individual experiments, including the one described here.

## 2.2. Experimental Procedure

To perform the experiment, students cooled a sample of the acid solution to 0°C using an ice bath. The sample was then allowed to warm to room temperature with constant stirring through gentle heating, use of a warm water bath, or simply removal of the ice bath. As the solution warmed, the students took pairs of pH and temperature measurements at different intervals until they had at least five different data points. From the pH, students calculated the  $[H^+]$  in the solution, which was used to calculate the  $K_a$  of the acid at that temperature. The students then prepared a van't Hoff plot ( $\ln K$  vs.  $1/T$ ) from which the thermodynamic values  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and y-intercept, respectively, of the linear trend line produced by a linear regression analysis using Excel. From these quantities, the  $\Delta G^\circ$  (at 25.0 °C) was calculated, so that all three major thermodynamic quantities were determined from measurements of pH and temperature.

Students were provided a sample (50 mL) of the acid solution to perform the analysis (the volume of acid was chosen to correlate with the 100 mL beaker that had to be used in order to accommodate both the pH and temperature probes, while still allowing for a magnetic stir bar). Students were instructed to take pH/temperature readings at different intervals, but not to exceed a total change of more than 10°C (*vide infra*). Once the experimental run was concluded, the pH of the solution was adjusted until approximately neutral and then rinsed down the drain.

### 2.2.1. Experimental Conditions

The experiment was performed using MeasureNet Technology pH and temperature probes, though any pH probe or thermocouple/thermometer could be readily used. Using the MeasureNet Technology, the pH and temperature values are simultaneously displayed on a digital readout, while a thermometer can be read in tandem with pH measurements depending on the equipment available. It is also recommended to have a heating and stirring source, but neither of these are essential. It should also be noted that students in this laboratory curriculum work in groups to complete their experiments, though a student working alone should encounter no great difficulty with this procedure. While the technology constraints on this experiment are quite low, pH meters must have a resolution of at least 0.01 units to detect the changes in pH over the temperature ranges explored. To expedite the data acquisition, the weak acid solutions provided to students can be chilled prior to the start of lab.

## 2.3. Hazards

Glacial acetic acid is flammable, corrosive, a respiratory irritant, and can cause organ damage through prolonged or repeated exposure according to the SDS obtained from Fisher Scientific. The acetic acid solutions used in this experiment are diluted, reducing the risk to students.

## 3. Results & Discussion

### 3.1. Calculated Quantities

The concentration of acetic acid (1 M) was chosen such that the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  determined were the standard values. Due to the nature of the experimental procedure, the  $\Delta H^\circ$  and  $\Delta S^\circ$  values are not defined by their exact temperatures, but the value of  $\Delta G^\circ$  is calculated at 298 K ( $\Delta G^\circ_{298}$ ).

### 3.2. Student Results

Data obtained from 95 groups of students was subjected to statistical analysis to eliminate potential outliers (see Supporting Information). Of the 95 sets of data submitted, only nine (9.5%) of the data sets were judged as outliers for the  $\Delta H^\circ$  and  $\Delta S^\circ$  values. After removal of these outliers, the  $\Delta G^\circ_{298}$  values were subjected to the same analysis, producing an additional five outliers, representing 5.8% of the remaining population. This is a

positive indication that the experiment is robust enough to be successful with a wide range of student skill levels. After statistical analysis, the following values were obtained (errors given to one standard deviation):  $\Delta H^\circ = 67.8 \pm 24.5$  kJ/mol;  $\Delta S^\circ = 147 \pm 91$  J/mol·K;  $\Delta G^\circ_{298} = 23.2 \pm 3.2$  kJ/mol. An example of typical student data and the corresponding van't Hoff plot are shown in Table 1 and Figure 1, respectively.

Table 1. Representative Student Data

T (°C)	pH
8.00	2.62
9.00	2.61
10.00	2.60
11.00	2.59
12.00	2.57

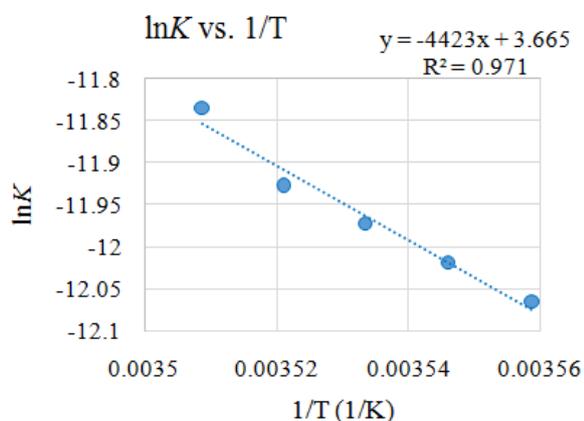


Figure 1. Representative van't Hoff plot ( $\ln K$  vs.  $1/T$ ) utilizing student data from Table 1

### 3.3. Interpretation of Results

While using equations (2) and (3), it is generally assumed that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary significantly with temperature, though this is not the case for the dissociation of acetic acid. [14] For this reason, the students were instructed to maintain their pH readings within a maximum range of 10 °C, although failure to adhere to this constraint did not appear to have an adverse effect on the calculated value of  $\Delta G^\circ_{298}$ . The variable temperature intervals over which the  $\Delta H^\circ$  and  $\Delta S^\circ$  values are calculated lead to error in those values, though the numerical results are consistent with the conceptual underpinnings. In this case, the vast majority of the  $\Delta G^\circ_{298}$  values (which have considerably less error due to the consistent temperature) are consistent with the non-spontaneous dissociation of the weak acid, leading to the appropriate conceptual conclusions regarding the data obtained. The calculated  $\Delta G^\circ_{298}$  of 23.2 kJ/mol compares favorably with the literature value of 26.6 kJ/mol [13].

All of the overall results are internally consistent with the observed data. As the temperature of the solution increases, the pH of the solution decreases, indicating an increased  $[H^+]$  and thus a greater dissociation of the acid. Since both  $\Delta H^\circ$  and  $\Delta S^\circ$  are positive, the reaction should be more spontaneous (proceed in the forward direction to a greater extent) as the temperature increases, as is observed.

Instructors can use the data and constructed van't Hoff plots to engage the students in conversations ranging from the fundamental bridge between the concepts of equilibrium and thermodynamics to more advanced applications utilizing LeChâtelier's Principle. When introducing the concept of LeChâtelier's Principle, it is usually generalized that increasing the temperature on an endothermic reaction will shift the direction (and magnitude) of the equilibrium toward the products side of the reaction, and toward the reactants in an exothermic reaction.

The student success rate on two separate questions on an ACS full-term exam evaluating the relationship between equilibrium and thermodynamics (Q1) and acid-base equilibria (Q2) are compared in Table 2. These results suggest that the experiment was successful in achieving the desired outcomes.

Table 2. Summary of Student Success Rates on Selected Questions from an ACS Standard Exam

Year	Q1 Success Rate	Q2 Success Rate
Y1	41.76%	46.89%
Y2	37.91%	50.00%
Y3	42.86%	59.02%

Student response to the experiment is generally positive. Of the 193 total respondents, 75 students identified the experiment as being "helpful, fun, interesting, or otherwise enjoyable", whereas only 26 students (the second-lowest total for any of the experiments performed) responded that the experiment was "unhelpful, boring, uninteresting, or otherwise unenjoyable".

## 4. Conclusion

An experimental procedure was developed to calculate the three key thermodynamic values ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ) through equilibrium constants determined using only pH and temperature measurements. The signs of the thermodynamic values are consistent with the underlying concepts of equilibrium and thermodynamics, allowing for the link between the topics to be discussed in general terms or in great detail. Student success rates increased on questions related to the topics explored as part of the experiment, and students generally perceived the experiment favorably.

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