

## **2006-2281: ENHANCING UNDERSTANDING OF EQUILIBRIUM CONCEPTS IN GENERAL CHEMISTRY USING THE SYSTEMATIC METHOD**

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## **Enhancing Understanding of Equilibrium Concepts in General Chemistry using the Systematic Method**

### **Abstract**

This study investigates an alternative to the commonly used concentration table method for describing chemical equilibria in General Chemistry. The concentration table method is arguably the single most difficult concept for students in this course. The difficulties arise from the number of simplifying assumptions that need to be made. Furthermore, once the problem has been simplified, a significant amount of time is often required for algebraic manipulations, which students in General Chemistry find difficult. As discussed in this paper, it is possible to deal with equilibrium in a more contemporary, holistic approach, where equilibrium expressions, charge, and mass balance equations are solved simultaneously. Such methods reduce the number of assumptions that need to be made to solve a given problem, and when solved using a symbolic computer algebra program, provide a reduction in the amount of work required to reach a numerical solution. Also, since multiple equilibrium reactions are no more difficult to solve than single reactions, students gain a more complete understanding of chemical equilibrium systems. In this study, we present preliminary results from a pilot study in which several different sections in our General Chemistry course are taught using the systematic method. Student understanding of key chemical concepts is monitored and compared to sections which are taught in the traditional manner. Student attitudes are also assessed in terms of perceived difficulties in learning the new method as well as student comfort with working with technology to solve problems. At present, we can state that no significant degradation in student scores is observed. Students in the test sections seem to be performing the same as or slightly above their peers in the standard sections.

### **Introduction**

General chemistry is an important foundational course for engineering studies. This is particularly true for chemical, environmental, and mechanical engineering, but all disciplines rely on general chemistry to varying degrees. Certainly, all four-year engineering programs begin with general chemistry in the freshman year. An important area of study within general chemistry focuses on the concept of chemical equilibrium. Weak aqueous acids and bases, precipitation equilibria, and gas-phase equilibria are standard topics. Students are taught to calculate equilibrium concentrations given total concentrations and equilibrium constants for the relevant reactions.

For determining equilibrium concentrations in reacting systems, the method that is currently taught is to write a concentration table to describe the reaction, and then solve for the unknown concentrations in the table by substitution into the equilibrium expression. This method is demonstrated below for a weak monoprotic acid, written

generically as HA. The initial concentration of acid is F moles per liter, and the numerical values for F and  $K_a$  are assumed to be known. The governing equilibrium reaction and the resulting concentration table are given below:

	$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$		
initial:	F	0	0
change:	-x	+x	+x
equilibrium:	F-x	x	x

*Equilibrium Expression:* 
$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})] \cdot [\text{A}^-(\text{aq})]}{[\text{HA(aq)}]} = \frac{x^2}{F - x}$$

The table is completed in steps, starting with writing the initial concentrations under the corresponding terms in the reaction. Chemical stoichiometry is used to complete the change line, which is usually written in terms of an unknown, x, which is negative for reactants and positive for products. The equilibrium line is just the difference between the initial concentrations and the change. The equilibrium terms are substituted back into the equilibrium expression, and the students solve the resulting equilibrium expression for x. It is important to point out that charge conservation is completely ignored in this method, autoionization of water is ignored, and simultaneous reactions need to be treated individually.

The method is conceptually simple, yet the algebra is difficult [1,2] for the average General Chemistry student. Relatively few mathematically-skilled students can solve an equilibrium expression that involves the solution of a cubic or higher order polynomial. The difficulty in teaching the algebra is compounded by well-entrenched chemistry teaching methods that attempt to simplify the equilibrium expression by first determining if x is small with respect to F. The goal is to reduce the polynomial to linear form, allowing for a more rapid solution. This method is simply a hold-over from pre-computer days when calculations had to lend themselves more readily to slide rules or pencil-and-paper.

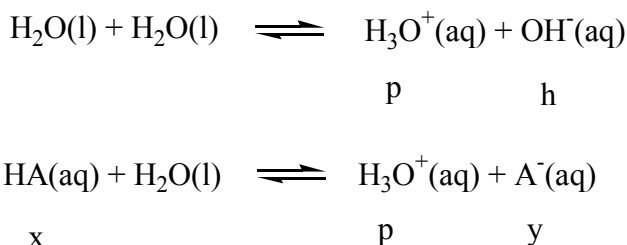
While it is true that these algebraic skills should not present great difficulty to students who are aspiring engineers, it should be recognized that the algebra is superimposed on abstract chemical topics which many college freshman are seeing for the first time. Furthermore, the algebra gets in the way of more relevant chemical concepts. In this paper, we are proposing an alternative method for teaching equilibrium concepts that is more firmly rooted in chemical and physical theory, requires minimal simplifying assumptions, and allows integration of computer technology directly into the classroom.

### Systematic Approach

In the “systematic approach[3-4]” to solving equilibrium problems, the student first develops a list of the governing chemical equilibria that describe the chemical

system. Once the reacting species have been identified, the equilibrium expressions for each reaction are written, followed by equations that describe conservation of charge and mass. Usually more than one independent mass balance can be written, so the idea is to write balance equations until the number of degrees of freedom is sufficiently reduced. The resulting system of equations is then solved.

Consider an example of a typical weak acid-base equilibrium problem of the type taught in General Chemistry. Specifically, given a weak monoprotic aqueous acid HA with concentration  $F$  mol/L, determine the  $[H_3O^+(aq)]$  and pH of the solution. The governing equilibrium reactions are given below.



*Equilibrium Expressions:*

$$K_w = p \cdot h$$

$$K_a = \frac{p \cdot y}{x}$$

*Charge Balance:*

$$p = h + y$$

*Mole Balance (on A):*

$$F = x + y$$

The quantities  $x$  and  $y$  are the concentrations of weak acid  $[HA(aq)]$  and its conjugate base  $[A^-(aq)]$ , and  $p$  and  $h$  are  $[H_3O^+(aq)]$  and  $[OH^-(aq)]$  respectively. The charge balance is simply a statement of the electrical neutrality of the solution. That is, the sum of the concentrations of all positive ions must equal the sum of concentrations of all negative ions. In other words,  $[+] = [-]$ . The total molar concentration of acid is  $F$ , which must equal the sum of  $[HA(aq)]$  and  $[A^-(aq)]$ .

The Mathematica implementation of the system of equations as well as the solution are shown in Figure 1. Note that we solve the system symbolically first, and then “numericize” the solution for the special cases we are interested in. In practical terms this is crucial. Students do not need to spend any time determining initial guesses for numerical solutions. Nor do they need to simplify the algebraic expressions prior to solution by making physical or chemical approximations.

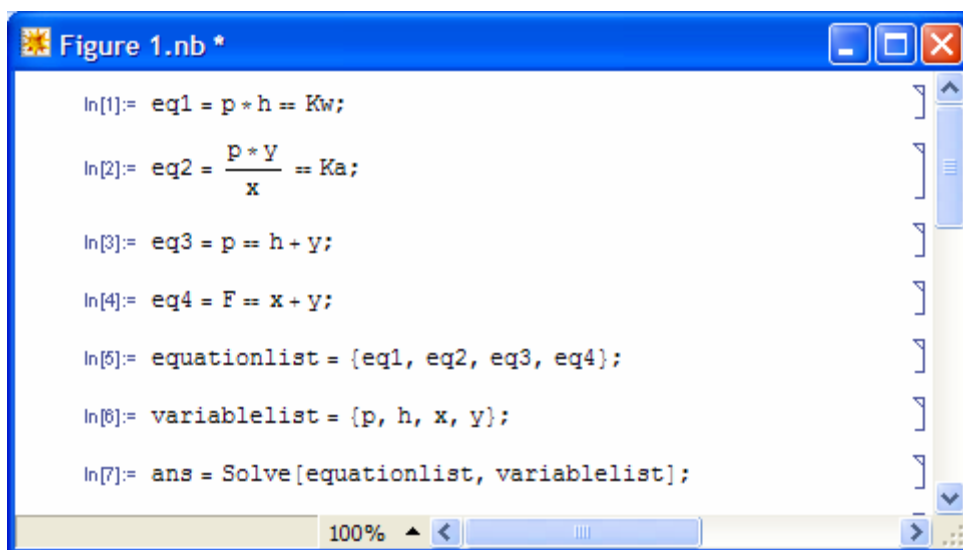


Figure 1. Mathematica 5.2 implementation of the systematic approach to solving the weak monoprotic acid equilibrium problem.

Figure 2 shows representative numerical output for  $F=0.01$  M,  $K_a=1.75 \times 10^{-5}$ , and  $K_w=1.01 \times 10^{-14}$ . The student must select the correct answer by eliminating any answers with negative real terms, since negative concentrations are not allowed. They must also eliminate terms with significant imaginary components, since concentrations are positive and real. The list of final answers is highlighted in the Figure.

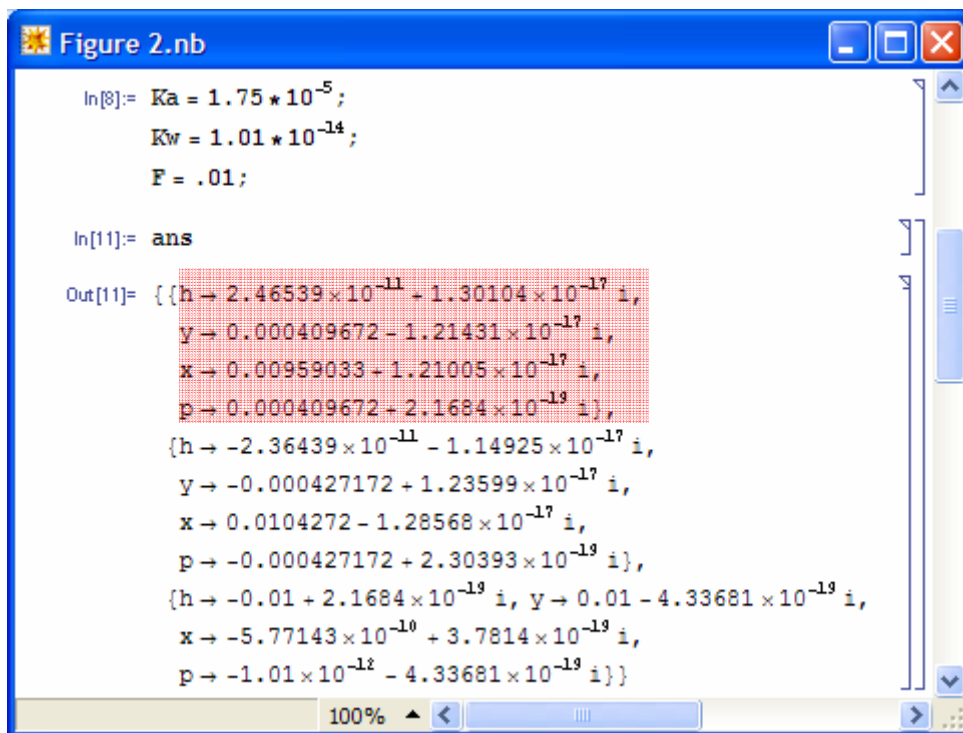


Figure 2. Screen shot of how one might “numericize” the output contained in “ans” to perform an actual computation.

Since the results are computerized, the data can be further analyzed by building a function that can be called repetitively under many different sets of conditions. This allows the student to further explore the system without the need to re-solve the original system of equations. An example is shown in Figure 3, where we evaluate the proton concentration and pH of the solution, since these variables are often studied in chemistry courses. Since the functions depend on  $F$ ,  $K_a$  and  $K_w$ , students can plot the results or make tables, or just enter the function over and over again.

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In[7]:= ans = Solve[equationlist, variablelist];

In[8]:= p[F_, Ka_, Kw_] = p /. ans;

In[9]:= p[.01, 1.75 * 10-5, 1.01 * 10-14]

Out[9]= {0.000409672 + 2.1684 × 10-19 i,
         -0.000427172 + 2.30393 × 10-19 i,
         -1.01 × 10-12 - 4.33681 × 10-19 i}

In[10]:= pH[F_, Ka_, Kw_] = -Log[10, Re[p /. ans][[1]]];

In[11]:= pH[.01, 1.75 * 10-5, 1.01 * 10-14]

Out[11]= 3.38756

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Figure 3. Screen shot of analytical function for examining the weak monoprotic acid system.

The mathematical method used here is not new. However, to implement this method without the use of a computer algebra program requires a significant amount of algebra. This is not an advantage for the vast majority of students who are already struggling with simple polynomials. Chemistry instructors have not adopted this method largely for this reason. However, the method is very simple to implement in symbolic math programs such as Mathematica.

We have initiated a pilot study to gauge the feasibility of using the Systematic/Mathematica approach in our General Chemistry course. Specifically, we attempt to address the following questions: 1) Does the systematic method enhance student understanding of equilibrium concepts with respect to traditional teaching methods? If so, what are the specific factors that contribute to the improvements? 2) Does the incorporation of a math solver, used from the student-owned laptop computer, make students more comfortable with using computers and technology to solve problems? 3) What are the major implementation issues involved with using this method on a course-wide basis? Each of these questions will be addressed in detail in our presentation.

The possible educational advantages to this approach may be significant. First, students make no simplifying assumptions regarding which equilibrium reactions to

include in the analysis, or which concentration terms should be neglected. If a reaction or concentration term is questionable, they can explore the conditions under which it can be removed. Second, the solution, once performed successfully, is completely automated. This means that the students can examine the solution from many different points of view and ask probative questions regarding the nature of the system. Third, extension to titration chemistry is relatively straightforward. Once the pH function is created, we can insert concentrations and volumes of acid and base into the charge and mass balance equations to generate complete titration curves. Additional examples of this will be included in our presentation.

## Methods

The conditions of the study are outlined here. All cadets at the Academy take the same General Chemistry course. There is a total population of approximately 1200 cadets enrolled in the course. The course is divided into small sections, averaging 40 to 80 cadets per section, with one instructor per section. The sections are further divided into hours, with approximately 20 cadets assigned to each hour. This means that the total instructor population is approximately 20, and each instructor teaches from two to four hours. Cadets enrolled in the course are partitioned into different hours based on ability, as measured by overall scores in the first semester. The highest-scoring cadets are pooled into nine “high” hours, and the lowest-scoring cadets are pooled into eight “low” hours. The remaining cadets go into “medium” hours. This sectioning process is done in order to address the learning pace of the cadets more efficiently. In this study, two “medium” hours and “high” hour were selected as test groups. Each of these hours were taught by different instructors, and each instructor was also responsible for standard (nontest) hours.

The cadets range in age from 18 to 21, most of them have had no prior college chemistry. However, some cadets have studied at the college level prior to arriving at West Point, and many have taken AP chemistry in high school. The average SAT score for the class of 2008 is 1280 (630 verbal, 650 math). All cadets have a personal laptop computer that they bring to class, and all cadets have Mathematica installed on their computer. The classrooms are equipped with a wireless network and a projector, and the instructors use SynchronEyes [5] Software to monitor progress, and to project work onto a classroom screen. To monitor the progress of the study, the study group took the same exams as the general course population, and certain problems were compared to gauge understanding of key equilibrium concepts. We also administered a survey to determine student attitudes toward use of technology.

Instructors for the general chemistry course typically come from various academic disciplines, including chemistry, chemical engineering, and the life sciences. Three instructors with various academic experience and backgrounds were chosen for this study. The experience and background of the instructors ranged from new instructor to twelve years teaching experience. Prior knowledge of Mathematica also varied from instructor to instructor, from almost no experience to considerable working knowledge.

The extreme background of these instructors was selected intentionally to gauge whether instructor background would be important in teaching the method.

To provide an appropriate teaching base for the systematic method, we took several steps to resource our test instructors and students. Several systematic method handouts with descriptive text and example problems were prepared that supplemented or replaced sections in the General Chemistry textbook. Homework problems, board (or recitation) problems, lab handouts and lab worksheets were also more appropriately aligned with the systematic method. Several meetings were held to discuss teaching strategies with our systematic method instructors. Despite all this work, the “table method approach” was far more resourced during our study, including descriptive sections in our General Chemistry textbook and web-based resources describing the table method approach. When analyzing the results of this study, one must consider the disparity in resources as well as the natural influence of 53 “test” cadets living with and perhaps even studying with the other 1100 “table method” cadets.

## Results and Discussion

The results of the entrance survey, as well as the survey questions, are shown in Table 1. The first question asked the students to rate different methods used for problem solving, ranging from technology-free to use of computer algebra software. The responses to the questions clearly show that the preferred method for solving problems is to use pencil and paper with a calculator, with scores of 4.37 and 4.58 out of a possible maximum score of 5.00. Excel is ranked somewhat lower at 3.17, and Mathematica received a very low score of 2.06. This is significant, since all cadets use Mathematica in the previous semester in their math courses. The other result that is interesting in this table is that although cadets are comfortable using the computer to solve problems (3.84/5.00), they do not use Mathematica outside of math class (1.81/5.00), nor do they see it as relevant (2.19/5.00). This is a highly surprising result given the enormous computational power present in the program.

The results of the first examination are summarized in Table 2. Results are reported for each individual instructor, for each of the three problems, for the instructor’s test hour, and the instructor’s standard hours. Questions 9a and 9b in the table assessed the ability to write an equilibrium expression given a chemical equilibrium reaction. These problems were graded using a cut scale that assessed each term in the numerator and denominator of the expression, as well as the exponents for each term. Question D was a complete problem of the type shown in Figure 1 above, using gas-phase reaction chemistry. Standard hour students answered the question using the table method. Results are reported as a percentage score. Cut scales for Question D were adjusted to make the different parts of the problem equivalent in weight to those of the general population. We do recognize that there is likely to be some bias in this adjustment process, which provided the additional motivation to use common, unaltered problems such as 9a and 9b. In all cases, the test section scores were either statistically indistinguishable or somewhat higher than the instructor’s standard sections.



Although our initial results look promising, we do not feel the results are conclusive, particularly after only one examination. The statistical differences are insignificant in most cases. We are encouraged by the fact that none of the sections appears to be lower than their peers. Future results that show additional graded events as a function of time will be very informative. We also place a considerable amount of importance on student attitudes as reflected in Table 1. The follow-up survey, to be administered at the end of the semester, will tell us a great deal about whether we are able to improve student attitudes toward use of technology.

Question	Response
Please rank the following in terms of your preference for solving problems.	
Pencil and paper	$4.37 \pm 0.86$ (52)
Calculator	$4.58 \pm 0.67$ (52)
Excel	$3.17 \pm 1.06$ (52)
Mathematica	$2.06 \pm 1.23$ (52)
I am knowledgeable about equilibrium concepts in acid-base chemistry.	$2.80 \pm 0.72$ (51)
I am comfortable using computers in my academic classes.	$3.84 \pm 0.80$ (52)
I use Mathematica as a tool in solving problems outside of math class.	$1.81 \pm 0.95$ (52)
The use of Mathematica is relevant outside of my math class.	$2.19 \pm 1.01$ (52)

Table 1. Results of initial survey of cadets in the test hours, reported as mean  $\pm$  standard deviation (sample size). Cadets were asked to rank their response on a scale from 1 to 5, with 1 being the least favorable response and 5 being most favorable.

Instructor / Question	Instructor's test hour	Instructor's standard hours
A / 9a <sup>1</sup>	82.4 ± 39.3 (17)	55.6 ± 50.2 (54)
B / 9a <sup>1</sup>	35.3 ± 49.3 (17)	23.6 ± 42.9 (55)
C / 9a <sup>1</sup>	100.0 ± 0.0 (19)	100.0 ± 0.0 (20)
A / 9b <sup>2</sup>	82.4 ± 39.3 (17)	70.4 ± 46.1 (54)
B / 9b <sup>2</sup>	29.4 ± 47.0 (17)	29.1 ± 45.8 (55)
C / 9b <sup>2</sup>	84.2 ± 37.5 (19)	100.0 ± 0.0 (20)
A / D <sup>3</sup>	78.8 ± 19.7 (17)	70.9 ± 22.3 (35)
B / D <sup>3</sup>	88.3 ± 10.3 (12)	70.8 ± 22.9 (43)
C / D <sup>3</sup>	87.4 ± 22.6 (19)	91.3 ± 5.0 (20)

<sup>1</sup> Equilibrium constant expression K from common exam questions.

<sup>2</sup> Equilibrium quotient expression Q from common exam questions.

<sup>3</sup> Multiconcept equilibrium problem.

Table 2. Results from Examination 1, reported as mean ± standard deviation (sample size). Results are shown for the instructor's test and standard hours.

## References

1. Hawkes, S.J., *J. Chem. Ed.*, 2003, 80, 1381.
2. Lewis, D.L., *J. Chem. Ed.*, 2004, 81, 1265.
3. de Levie, R. *Aqueous Acid-Base Equilibria and Titrations*; New York: Oxford University Press, 1999.
4. Harris, D.C. *Quantitative Chemical Analysis, 6<sup>th</sup> Edition*; New York: W.H. Freeman and Company, 2003, pp. 162-177.
5. Synchroneyes 5.1 by SMART Technologies, 1995-2004.