Using a Spreadsheet to Introduce Aqueous-Speciation Calculations to Geochemistry Students

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ABSTRACT
Software packages are commonly used to calculate the concentrations of aqueous species and to model mass transfer in geological systems. Because calculating the concentrations of all species in a simple fluid composition is difficult, many students focus on using the modeling software without understanding the underlying principles. Writing a spreadsheet program to calculate the distribution of aqueous species in a simple fluid composition requires students to understand the fundamental principles that describe fluid equilibria. Students also learn computational techniques used in modeling software and improve their spreadsheet-programming skills.

Keywords: Education – computer assisted; geochemistry; hydrogeology and hydrology; miscellaneous and mathematical geology.

Introduction
Elements dissolved in fluids occur as bare ions and aqueous complexes. The presence of aqueous complexes can increase mineral solubility, favor or inhibit ion adsorption, and affect metal toxicity and bioavailability (Langmuir, 1997). Therefore, it is important to measure the total concentration of elements in a fluid and to calculate the concentration of all species present.

A number of software packages are available to compute the distribution of aqueous species given a chemical analysis and the appropriate thermodynamic data (Worley 1979, 1983; Parkhurst, 1995). The concentration of aqueous species is computed by solving the non-linear equations representing the conservation of mass and energy in the fluid. These equations are complex even for simple systems. For this reason, students often view such software as a black box that produces "the answer" and are more interested in learning the mechanics of using the software than in learning the principles upon which the software is based. Furthermore, they remain unaware of the computational error that inevitably appears during the solution of the equations.

Student understanding of the methods used to compute the distribution of aqueous species and the underlying geochemical principles can be improved by having them prepare a spreadsheet-distribution program. This approach has several advantages (Martin, 1993). Students must understand the underlying conservation equations before they begin programming, and they also are led to realize the importance of simplifying assumptions, significant figures, and computational errors. Furthermore, they improve their spreadsheet-programming skills.

In this paper, an iterative technique for calculating the distribution of aqueous species in a simple fluid using a spreadsheet is presented. The fundamental equations underlying this method are explained, and a convenient method for solving the equations using spreadsheets is presented. Finally, use of the exercise in a second-semester geochemistry course is discussed.

Theoretical Foundation
The concentration of the species in a fluid can be calculated given the fluid's pH, a chemical analysis, and the equilibrium constants for reactions among the various aqueous species (Wolery, 1979; 1983). In this paper, solutions to equations describing equilibria in the fluid are obtained iteratively (van Zeijgeren and Storey, 1970) as described by Knight (1974). To simplify the computations, it is assumed that each element is present in a single valence state and all species behave ideally.

The iterative technique is relatively simple (Figure 1). Concentrations of H+ and OH− are calculated from the fluid's pH, one element is selected as the charge-balance element, and a basis species is chosen for each element. Because the concentrations of all other species are calculated from the concentrations of basis species, the basis species selected for each element is the species having the highest concentration of that element. For most systems at the earth's surface, bare ions are selected as basis species. The basis species can be changed if the selected species is not the most abundant species containing a given element.

For the first iteration, the concentration of each basis species, except the charge-balance basis species, is set equal to the concentration of the element it represents. The concentration of the charge-balance basis species is adjusted to maintain electrical neutrality. Concentrations of all remaining species are determined by sequentially working through each element, iteratively calculating the concentration of all species containing that element. When all elements are complete, the entire process is repeated, using the basis-species concentrations calculated in the previous step, until mass and energy conservation equations are satisfied for all elements.

Concentrations of non-basis species are represented as a function of basis-species concentrations. First, a mass-conservation expression is written for an element. The concentrations of non-basis species containing
that element are expressed in terms of the appropriate equilibrium constants and the concentrations of basis species. A revised basis-species concentration is obtained and used to update the concentrations of non-basis species containing that element. The concentration of the charge-balance basis species is adjusted to achieve electrical neutrality, and the process is repeated until the concentration of the basis species converges. When one element is complete, concentrations of species containing the next element are revised using the concentration of the basis species obtained from the previous element (Figure 1).

Consider a fluid having a pH of 5 and containing Na, Cl, Ca, H, and O. The measured concentrations of Cl and Ca are 1.0 and 0.01 moles/kg, respectively, and Na is the charge-balance element. Aqueous species present are Na⁺, NaCl⁺, Cl⁻, Ca²⁺, CaCl₂, H⁺, OH⁻, and H₂O. Basis species for Na, Cl, and Ca are Na⁺, Cl⁻, Ca²⁺, respectively.

For the first iteration, the concentration of each basis species, except Na⁺, is set to the concentration of the element it represents,

\[ m_{Cl^-} = m_{Ca^2+} = 1.000 \]

and

\[ m_{Na^+} = m_{Cl^-} = 0.010 \]

where \( m_{Cl^-} \) is the concentration of Cl⁻ and \( m_{Ca^2+} \) is the total concentration of chlorine. Concentrations of H⁺ and OH⁻ are set by the pH,

\[ m_{H^+} = 10^{-pH} = 10^{-5} \]

and

\[ m_{OH^-} = K_{H_2O} / m_{H^+} = 10^{-14} / 10^{-5} = 10^{-9} \]

The concentration of Na⁺ is set to achieve electrical neutrality,

\[ m_{Na^+} = m_{Cl^-} + m_{Ca^2+} - (2m_{Ca^2+} + m_{H^+} + m_{CaCl_2}) = 0.980 \text{ moles/kg}. \]

The concentrations of the non-basis species are obtained by writing a mass-conservation expression for each element exclusive of H, O, and Na (the charge-balance element),

\[ m_{Cl^-} = m_{Cl^-} + m_{NaCl^+} + m_{CaCl_2} - 2m_{CaCl_2} \]

and

\[ m_{Ca^2+} = m_{Ca^2+} + m_{NaCl^+} + m_{CaCl_2} \]

Ratios relating the concentration of each species to the concentrations of basis species are substituted into the mass-balance equations. Equation 6 becomes

\[ m_{Cl^-} = m_{Cl^-} \left( m_{CaCl_2} + m_{NaCl^+} / m_{Cl^-} + 2m_{CaCl_2} / m_{Cl^-} \right) \]

and

\[ m_{CaCl_2} = m_{CaCl_2} (1 + R_{NaCl^+} + R_{CaCl_2} + 2R_{CaCl_2}) \]

Figure 1. Flowchart describing the algorithm used to calculate the distribution of aqueous species.

where \( R_{NaCl^+} = \frac{m_{NaCl^+}}{m_{Cl^-}} \). Equation 8 can be rearranged as follows to solve for \( m_{Cl^-} \):

\[ m_{Cl^-} = m_{Cl^-} (1 + R_{NaCl^+} + R_{CaCl_2} + 2R_{CaCl_2}) \]

Ratios in Equation 9 are evaluated by writing reactions in which 1 mole of the non-basis species reacts to produce basis species. For Ca-bearing species, the appropriate reactions are

\[ NaCl^+ \rightleftharpoons Na^+ + Cl^- \]

\[ CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^- \]

and

\[ CaCl^- \rightleftharpoons Ca^{2+} + Cl^- \]
Using a Spreadsheet to Introduce Aqueous-Speciation Calculations to Geochemistry Students

<table>
<thead>
<tr>
<th>Reaction</th>
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<tbody>
<tr>
<td>NaCl(aq) ⇌ Na⁺ + Cl⁻</td>
<td>5.99</td>
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<tr>
<td>CaCl₂(s) ⇌ Ca⁺² + 2Cl⁻</td>
<td>5.14</td>
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<tr>
<td>CaCl⁺ ⇌ Ca⁺² + Cl⁻</td>
<td>0.76</td>
</tr>
<tr>
<td>H₂O ⇌ H⁺ + OH⁻</td>
<td>10⁻¹⁷</td>
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Table 1. Equilibrium constants for dissociation reactions
(Calculated using SUPCRT92; Johnson and others, 1992).

The ratios in Equation 9 can be expressed as a function of equilibrium constants for reactions 10-12 (Table 1), as follows.

\[
K_{NaCl} = \frac{m_{NaCl}}{m_{Na⁺} m_{Cl⁻}}. 
\]

\[
R_{NaCl} = \frac{m_{NaCl}}{m_{Cl⁻}} = \frac{0.980}{5.990} = 0.164. \tag{13}
\]

\[
K_{CaCl₂} = \frac{m_{CaCl₂}}{m_{Ca⁺²} m_{Cl⁻}}. 
\]

\[
R_{CaCl₂} = \frac{m_{CaCl₂}}{m_{Cl⁻}} = \frac{0.01}{5.137} = 1.95 \times 10^{-3}. \tag{14}
\]

\[
K_{CaCl⁺} = \frac{m_{CaCl⁺}}{m_{Ca⁺²} m_{Cl⁻}}. 
\]

\[
R_{CaCl⁺} = \frac{m_{CaCl⁺}}{m_{Cl⁻}} = 0.01 = 1.95 \times 10^{-3}. \tag{15}
\]

These values are substituted into Equation 9, which is solved to obtain a revised concentration of Cl⁻, as follows.

\[
m_{Cl⁻} = m_{Cl⁻}^r (1 + R_{NaCl} + R_{CaCl₂} + 2R_{CaCl⁺})^{-1} 
= 1.0(1 + 0.164 + 1.95 \times 10^{-3} + 2(1.31 \times 10^{-3}))^{-1} 
= 0.839 \text{ moles/kg}. \tag{16}
\]

The concentration of all non-basis species containing chlorine can be calculated using the revised value of \(m_{Cl⁻}\) and the ratios defined in Equation 8.

\[
m_{NaCl(aq)} = R_{NaCl} m_{Cl⁻} = (0.164)(0.839) = 0.137 \text{ moles/kg}. \tag{17}
\]

\[
m_{CaCl₂} = R_{CaCl₂} m_{Cl⁻} = (1.31 \times 10^{-3})(0.839) = 0.011 \text{ moles/kg}. \tag{18}
\]

\[
m_{CaCl⁺} = R_{CaCl⁺} m_{Cl⁻} = (1.95 \times 10^{-3})(0.839) = 0.002 \text{ moles/kg}. \tag{19}
\]

The value of \(m_{Cl⁻}(0.839 \text{ moles/kg})\) obtained from Equation 16 is compared to the previous value (1.000 moles/kg). If the two are sufficiently close, the mass-balance expression for chlorine is satisfied. If the values differ, the value of \(m_{Cl⁻}\) obtained above (0.839 moles/kg) is used to recalculate the ratios in Equations 13-15. The recalculated ratios are then used to calculate a new value for \(m_{Cl⁻}\). These steps are repeated until \(m_{Cl⁻}\) converges.

The example presented herein was chosen because \(m_{Cl⁻}\) converges to 0.859 moles/kg in a few iterations. However, rapid convergence is not always the case. In fluids where a large number of chlorine species are present and/or the ionic strength is high, values of \(m_{Cl⁻}\) obtained from successive iterations oscillate, and it may take 50 or more iterations to converge. These oscillations are illustrated in Figure 2, which shows values of \(m_{Cl⁻}\) calculated, as described above, for a fluid with a pH of 2 containing chlorine (0.100 moles/kg), potassium (0.010 moles/kg), and silver (0.001 moles/kg). A total of seven chloride species (Cl⁻, K⁺, Na⁺, Ag⁺, Ag⁺², AgCl⁺, AgCl⁺², AgCl⁺³) are present, and 50 iterations are required for \(m_{Cl⁻}\) to converge to 0.434 moles/kg.

The number of iterations required to achieve convergence can be reduced. For example, the average value of \(m_{Cl⁻}\) computed in the current and previous iteration can be used to calculate the ratios defined in Equation 8. This averaging technique in the silver-bearing fluid described above reduces the number of iterations needed for the value of \(m_{Cl⁻}\) to converge from 50 to 20 (Figure 2).

After the value of \(m_{Cl⁻}\) has converged, the next element is considered. The mass-balance expression for Ca (Equation 7) is expressed in terms of ratios, as follows.

\[
m_{Ca⁰} = m_{Ca^{+}} \left( \frac{m_{CaCl⁺}}{m_{Ca⁺²}} + \frac{m_{Ca^{+}}} {m_{Ca⁺²}} \right), \tag{18}
\]

\[
m_{Ca^{+}} = m_{Ca^{+}} (1 - R_{CaCl₂} + R_{CaCl⁺})^{-1}, \tag{19}
\]
Table 2. The spreadsheet, showing the concentration and ratio calculated for aqueous species at each iteration. See text for discussion.

![Table 2](image)

where

$$R_{CaCl_2} = \frac{m_{CaCl_2} - m_{Ca^2+}}{m_{Ca^2+}}$$

and

$$R_{Ca^{2+}} = \frac{m_{Ca^{2+}}}{m_{Ca^2+}}$$

The ratios obtained in Equations 21 and 22 are substituted into Equation 20 to obtain a revised value for $m_{Ca^{2+}}$. Values of $m_{CaCl_2}$ and $m_{Ca^{2+}}$ are updated using Equations 21 and 22, as follows.

$$m_{CaCl_2} = R_{CaCl_2} m_{Ca^2+}$$

and

$$m_{Ca^{2+}} = R_{Ca^{2+}} m_{Ca^2+}$$

Equations 20-24 are iteratively solved until the value of $m_{Ca^{2+}}$ converges.

Recalculating the concentration of Ca-bearing species changes the concentration of some Cl-bearing species (CaCl and CaCl$_{2w}$). In the example, the total concentration of Cl has decreased from 1.000 moles/kg to 0.989 moles/kg. To correct this discrepancy, it is necessary to cycle through all of the elements again until the concentrations of all species converge to a single value and the conservation-of-mass expression is satisfied for each element. In the example, convergence is achieved after only two additional iterations for Cl (Table 2).

### Setting up the Spreadsheet

The spreadsheet is organized in such a way that labels for the concentration and ratio of each species, the total concentration of each element, and charge balance are entered into Column A. Equilibrium constants for non-basis-species dissociation reactions are entered into Column B in the same row as the reactant species, and fluid composition is entered in the first row. Sample spreadsheets showing the numerical values and equations used in the example are shown in Tables 2 and 3, respectively. In the following discussion, refer to Table 3 for the appropriate cell(s) to enter each equation.

Information used in the first iteration is entered into Column C. The initial concentrations of basis species (Equations 1 and 2) are copied into the appropriate rows using the "^" notation in Excel. Equations used to calculate the concentrations of $H^+$ and $OH^-$ (Equations 3 and 4), and the charge of the fluid exclusive of $Na^+$ (Equation 5), are entered in the
Table 3. The spreadsheet, showing the formulas used to compute the values shown in Table 3. Arrows indicate that the contents of the cell in which the arrow originates should be copied to all other cells the arrow passes through. See text for discussion.

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Table 3. The spreadsheet, showing the formulas used to compute the values shown in Table 3. Arrows indicate that the contents of the cell in which the arrow originates should be copied to all other cells the arrow passes through. See text for discussion.

appropriate rows. The concentration of Na' is set equal to the opposite of the calculated charge to achieve electrical neutrality. Equations used to calculate the ratios for Cl-bearing species (Equations 13-15) are also entered into Column C, as are mass-balance equations for Na, Cl, and Ca (Equations 6 and 7).

Revised concentrations of Cl-bearing species are computed in Column D. Parameters used to revise the concentration of Cl (Equation 8) include the total concentration of Cl (Cell B1) and the ratios calculated in Column C. The concentrations of other Cl-bearing species, calculated from Equations 17-19, use the revised concentration of Cl in Column D and the ratios in Column C. All remaining values and equations in Column D are copied from Column C. The concentration of Cl in Cell D5 is compared to the concentration in Cell C5. If the values are not equivalent, Column D is copied and pasted into the adjacent columns until the concentration of Cl converges.

Using the average value of \( m_{\text{Cl}} \), obtained from the current and previous iteration, to calculate ratios for Cl-bearing species can result in faster convergence. In this case, the equation used to calculate the CaCl\(_{2}\) ratio in cell D20 is

\[(D^8*(C5+D5))/B10,\]

instead of

\[(D^8*D5)/B10.\]

Column D is then copied and pasted into the adjacent columns until the concentration of Cl converges.

Concentrations of aqueous species containing Ca are calculated next. The concentrations of all species calculated in the final Cl-iteration (Column G) are copied as initial values into Column H. Equations 21 and 22, defining Ca ratios, are also entered into Column H, and equations used to revise the concentrations of Ca-bearing species (Equations 20, 23 and 24) are entered into Column I. The concentrations of all species not containing Ca are copied from Column H into Column I. Column I can then be copied and pasted into adjacent columns until the concentration of Ca\(^{2+}\) converges.

The final three columns in Tables 2 and 3 contain the second iteration for Cl. The initial concentrations of all species are copied from Column K and the equations are copied from Column D. After only two iterations, the concentration of Cl converges to 0.866 moles/kg and the total concentration of Ca increases by only 1%.

Discussion
Second-semester geochemistry students were given an assignment to write a spreadsheet program to calculate the distribution of Pb-Cl species in an aqueous fluid. Class lectures covered the theoretical basis for the distribution of aqueous species and the Ca-Cl example presented herein. Students were given a copy of the spreadsheet in Table 2. However, they were not given the formulas in Table 3. To insure they understood the procedure, students first wrote a program to replicate the spreadsheet in Table 2. They then modified the program to calculate the distribution of the Pb-Cl species for a given fluid composition. After completing the assignment, students better understood the geochemical principles describing the formation of aqueous complexes and were able to use spreadsheets for iterative calculations.

Once the spreadsheet program is complete, it is easy to investigate how changing fluid composition affects the relative abundance of bare ions and complexed species in the fluid. For example, Figure 3 illustrates how the addition of chloride and calcium changes the relative amounts of CaCl$_2$ and CaCl$^-$ in a fluid. Lists of aqueous species for which thermodynamic data are available can be found in most geochemistry texts, making it relatively easy to design exercises to fit into any course.

Summary and Conclusions
Students in a second-semester geochemistry course were assigned a problem to write a spreadsheet program to calculate the distribution of aqueous species in a relatively simple fluid composition. Writing the program required students to understand the geochemical principles describing fluid equilibria and reinforced spreadsheet-programming skills. Students also became aware of the computational techniques used in speciation and mass-transport software and no longer view these programs as a black box.

Acknowledgments
I thank Jeff Snyder, Norm Levine, Bruce Gerke, Matt Pesci and two anonymous referees for detailed comments that vastly improved this manuscript.

References Cited

Figure 3. The mole percent of calcium-bearing species calculated as a function of the total chloride in the solution (top), and the mole percent of chloride species calculated as a function of the total calcium in the solution (bottom).