Interactive Java-based Web Site for Teaching Chemical Reaction Stoichiometry

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1 Introduction

Chemical reaction stoichiometry (CRS) is a branch of chemical stoichiometry dealing with the constraints, in the form of chemical equations, placed on changes in the composition of a closed reacting system by the requirement for conservation of the amount of each atomic species. This simple conservation concept has far-reaching consequences for all of chemistry and chemical engineering, including reaction kinetics and reactor design, reaction equilibrium, and reaction "book-keeping" in general. If chemical equations are to be used to express this concept, it is important to have a universal, systematic method for generating a proper set for *any* system under consideration. However, many methods currently in use, particularly in introductory teaching, do not properly or fully exploit the concept, and may give incomplete or misleading results; their scope is very limited, rendering them obsolete for general use.

To understand the role played by CRS, we believe that it is desirable to study it in its own right, "uncontaminated" by implications stemming from such things as reaction networks, reaction mechanisms, and equilibrium. Conversely, CRS does not contribute to intrinsic predictive information for kinetics or equilibrium, but only provides constraints on any predictions.

The universal, systematic method we describe in this paper and implement on the web site is not new, and has been described extensively elsewhere[1,2]. As an aid to the efficiency of learning new material, *i.e.*, CRS, it builds on a student's existing knowledge of very basic material (in addition to the concept of atomic conservation): the representation of a chemical species by a molecular formula, and the solution of sets of linear algebraic equations. For want of a better name, here we call it the *matrix reduction method* (MRM); it can be implemented by hand-calculation, and, for convenience in complex cases, can be easily programmed for implementation by computer. A new Java applet for the latter is introduced in this paper and on the web site.

In spite of a long history of the use of an algebraic method for the simplest situation in CRS, that of balancing a single specified reaction (method of Bottomley[3]), there appears to be considerable resistance on the part of instructors to the use of MRM in CRS. The reasons given are: (1) that it emphasizes mathematics and not chemistry, (2) that, as a result, students don't learn about chemistry in the form of "oxidation numbers" and "half-reactions", and (3) that, if implemented by computer, it uses a "sledgehammer" to "crack the egg" of (in many cases) a relatively simple problem. In response, it can be argued that (1) students learn precisely what part of chemistry is involved in CRS (see also Olson[4]), (2) other parts are extraneous to, and unnecessary for, CRS, and (3) use of computers and computer software is simply a matter of convenience to eliminate tedium in large-scale systems, but is not a necessity.

To overcome our suspicion of resistance on the part of many instructors, in this presentation, we are taking advantage of two advances in technology which may act as catalysts to achieve adoption of MRM: ease of accessibility afforded by a web site on a global basis, and the interactive capability of a Java applet for implementation of the method.

The purpose of this *paper* then is to describe a web site that can be used as a teaching/learning tool for CRS. The purpose of the *site*, in turn, is to use the world-wide web to provide a tutorial on CRS, an interactive tool to generate chemical equations, and a forum for discussion and exchange of information on CRS.

In the following parts of the paper, we first give some historical background on CRS, and then describe MRM for generating chemical equations, together with an example to illustrate solution by hand calculation. This is followed by a description of the web site contents in outline, a detailed description of the use of the Java applet, and an example to illustrate its use. We conclude by outlining our strategies for raising awareness of the web site, and for evaluating its efficacy, together with responses obtained to date.

2 Historical Background

Historically, it is perhaps natural that writing chemical equations in a stoichiometric sense arose from observed chemical reactions. This is particularly self-evident when the reacting system can be accurately represented by 1 reaction (*e.g.*, $2SO_2 + O_2 \rightarrow 2\ SO_3$); CRS is then expressed by 1 equation ($R = 1$; $2SO_2 + O_2 = 2\ SO_3$). The case of $R = 1$ is an important and relatively common one in inorganic industrial processes, analytical chemistry and electrochemistry. Probably for this reason, together with its simplicity, there has been an over-emphasis on this case in chemical pedagogy. In this pedagogy, CRS is reduced to the chemical "game" of how to "balance" a *specified* chemical reaction in skeletal form. The existence of many (and continuing) papers in the literature attests to the "popularity" of this game.

More generally, a reacting system may be specified by a *set* of skeletal chemical reactions, or by a *set* of chemical species (without reactions), either set normally including information

about the molecular formulas of the species involved. In either situation, two questions arise in CRS: (1) what is the proper number (R) of independent chemical equations? and (2) how can a *proper set* of R equations be obtained? The *a priori* specification of $R = 1$ for a system may be an *underspecification*, a situation of which there are many examples in the literature, most of them not realized, but sometimes described as "reactions that can be balanced in an infinite number of ways".

For the simple case of $R = 1$, a sufficient method to balance a specified chemical reaction was given 120 years ago by Bottomley[3]. This is sometimes referred to as the method of undetermined coefficients or the "algebraic" method. It is equivalent, for $R = 1$, to the method used here (MRM) in the Java applet, and can be extended to cases of $R > 1$ to make it completely equivalent to MRM[5]. Other methods used for a specified single reaction are: the method of inspection, the oxidation-number method (for inorganic and organic oxidation-reduction reactions), and the method of half-reactions (naturally tied to reactions in chemical cells). None of these methods addresses the question of the value of R, and the last two are inherently incapable of dealing with $R > 1$. Use of the method of inspection is "fair game" wherever it can be simply applied, but we consider the other two to be obsolete because of their limitations, which include their apparent inability to be programmed for computer implementation, and because the additional artifices, oxidation numbers and half-reactions, are unnecessary (in spite of their value outside CRS).

A number of authors have proposed computer programs for (1) $R = 1$, *i.e.*, for balancing a specified reaction in skeletal form, apparently all by means of the Bottomley method, and (2) $R \geq 1$, *i.e.*, for both determining R and generating a proper set of R equations. For $R = 1$, these include programs by Brown *et al.*[6], Rosen[7], Ramette[8], and Campanario[9]. For $R \geq 1$, they include programs by Smith and Missen[2,10], and by Betz *et al.*[11], all of which utilize MRM. In addition, Smith and Missen[12] have shown how computer algebra software, such as Mathematica and Maple, can be used to implement MRM. The Java applet made available on the web site described in this paper is a universally available interactive program implementing MRM for $R \geq 1$. We remark in passing that Wink[13] has presented a computer spreadsheet program that has some aspects in common with MRM, but which is not a universal method.

3 The Matrix Reduction Method (MRM) and a Hand Implementation Example

The matrix-reduction method (MRM) is a method for generating chemical equations for a reacting system specified by a list of species. MRM is what we define as a universal, systematic method: universal because it can be used for *any* chemical system ($R \geq 1$); and systematic because it can be described unambiguously in terms of a simple algorithm. Although it can be implemented by means of hand-calculation, for large systems, it is convenient to use a computer implementation of the MRM algorithm. In this section, we present the procedure for carrying out MRM as an algorithm, and use an example to illustrate its implementation

by hand calculation.

We describe the system by means of an ordered list of chemical species and the elements composing them. For example, the system composed of the species CH_4, O_2, CO_2, H_2O is represented by {(CH_4, CO_2, O_2, H_2O), (C, H, O)} (For a charged species such as Na^+, electronic charge is treated as an element, with the symbol p for the protonic charge; p = +1 for Na^+). The molecular formula of each species is represented as a column of subscripts, and the entire set of such formulas composes a matrix, called the *formula matrix* of the system. For the example quoted, the formula matrix is

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 4 & 0 & 0 & 2 \\ 0 & 2 & 2 & 1 \end{pmatrix}$$

The steps in the procedure to obtain a proper set of chemical equations for a system are as follows[1,2]:

1. Write the formula matrix $\mathbf{A}$ for the given system of N species and M elements. It is convenient to identify each column at the top by the chemical species represented.

2. Form a unit matrix as large as possible in the upper-left portion of $\mathbf{A}$ by means of elementary row operations, and column interchange if necessary; if columns are interchanged, the designations of the species (at the top) must be interchanged also. The final result is a matrix $\mathbf{A}^*$, called the unit matrix form of $\mathbf{A}$.

3. At the end of these steps, the following are established:

   - The rank of the matrix $\mathbf{A}$ is the number of 1's on the principal diagonal of $\mathbf{A}^*$; this is equal to C, the number of *component species*.
   - A set of component species is given by the C species above the columns of $\mathbf{A}^*$.
   - The maximum number of linearly independent chemical equations is given by $R = N - C$.
   - The coefficients of a proper set of chemical equations are obtained from the columns of the part of the matrix $\mathbf{A}^*$ to the right of the unit matrix; each column relates to the formation from the component species of one mole of the *noncomponent* species whose designation heads that column, and the entries in the column refer to the stoichiometric coefficients of the component species in the order of the component species columns in the unit matrix (this set of equations is said to be in *canonical form*).

This procedure can be implemented by hand-calculation for most cases that a student or instructor will encounter. This includes virtually all cases of single-equation systems ($R = 1$), such as are provided by complicated oxidation-reduction reactions. Even for cases when $R > 1$, the procedure is still feasible for hand-calculation. For very complex systems involving many species and elements, hand-calculation becomes tedious, and it is then more convenient to use a computer implementation of the procedure. The Java applet JSTOICH

presented on the web site implements MRM.

We illustrate the hand-calculation procedure with the system[14] {(ClO_2^-, H_3O^+, Cl_2, H_2O, ClO_3^-, ClO_2), (H, Cl, O, p)}

1.

$$\mathbf{A} = \begin{array}{c} \begin{array}{cccccc} ClO_2^- & H_3O^+ & Cl_2 & H_2O & ClO_3^- & ClO_2 \end{array} \\ \begin{pmatrix} 0 & 3 & 0 & 2 & 0 & 0 \\ 1 & 0 & 2 & 0 & 1 & 1 \\ 2 & 1 & 0 & 1 & 3 & 2 \\ -1 & 1 & 0 & 0 & -1 & 0 \end{pmatrix} \end{array}$$

2.

$$\mathbf{A}^* = \begin{array}{c} \begin{array}{cccccc} H_3O^+ & ClO_2^- & Cl_2 & H_2O & ClO_3^- & ClO_2 \end{array} \\ \begin{pmatrix} 1 & 0 & 0 & 0 & 2/3 & 4/3 \\ 0 & 1 & 0 & 0 & 5/3 & 4/3 \\ 0 & 0 & 1 & 0 & -1/3 & -1/6 \\ 0 & 0 & 0 & 1 & -1 & -2 \end{pmatrix} \end{array}$$

3.
- $\text{rank}(\mathbf{A}) = \text{rank}(\mathbf{A}^*) = 4 = C$
- component species: H_3O^+, ClO_2^-, Cl_2, H_2O
  noncomponent species: ClO_3^-, ClO_2
- $R = N - C = 6 - 4 = 2$
- The 2 chemical equations in canonical form are:

  (2/3)H_3O^+ + (5/3)ClO_2^- + (-1/3)Cl_2 + (-1)H_2O = (1)ClO_3^-
  (4/3)H_3O^+ + (4/3)ClO_2^- + (-1/6)Cl_2 + (-2)H_2O = (1)ClO_2
  or, in conventional canonical chemical form:
  $2H_3O^+ + 5ClO_2^- = 3ClO_3^- + Cl_2 + 3H_2O$
  $8H_3O^+ + 8ClO_2^- = 6ClO_2 + Cl_2 + 12H_2O$

4 Web Site Contents

The contents of the web site are shown in Figure 1, and are displayed by clicking on a link on the main Home Page of the site, located at
http://www.mathstat.uoguelph.ca/faculty/smith/stoich/. Hyperlinks are indicated by underlining. The first main section contains the tutorial, describes the computer implementations of MRM, including an example of the use of the Java applet, and provides further exercises in CRS for the user. The second main section gives resource material on CRS; this section is to be expanded in the future, as the result of feedback from the user community.

CONTENTS

Figure 1: Contents of the CRS web site at
http://www.mathstat.uoguelph.ca/faculty/smith/jstoich/

5 Use of the Java Applet

To implement JSTOICH, the steps are as follows:

1.
   - Enter the number of species and number of elements in initial window.
   - Click the OK button.

   A new window will appear for the entry of the species names and their molecular formulas in a table.

2.
   - Enter the species names in the first column as indicated, using any desired notation (*e.g.*, H2O(g) for gaseous water and H2O(l) for liquid water; i-C4H8 for isobutene, *etc.*).
   - Enter the names of the elements across the top row of the table, using any desired notation (*e.g.*, Na for sodium, H for hydrogen, *etc.*).
   - Enter the (total) subscripts to each of the elements for each species in the row of the table to the right of its name (*e.g.*, for H_2O, enter 2 for H, 1 for O, and 0 for any other element in the system; for $(CH_3)_2CO$ enter 3 for C, 6 for H, 1 for O, and 0 for any other element in the system.)
   - Click the Calculate button.

   The window is over-written with the results of the calculation.

3. The window contains:

   - C, the number of components
   - R, the number of independent chemical equations in a proper set
   - a proper set of chemical equations in conventional canonical chemical form.
   - the component species indicated in the equations in blue, and the noncomponent species indicated in the usual text color, typically black.

Figures 2-4 show the three windows for the example problem[15] {(NH_4ClO_4, Cl_2, N_2O, NOCl, HCl, H_2O, N_2, O_2, ClO_2), (N, H, Cl, O)}, relating to the explosion of ammonium perchlorate.

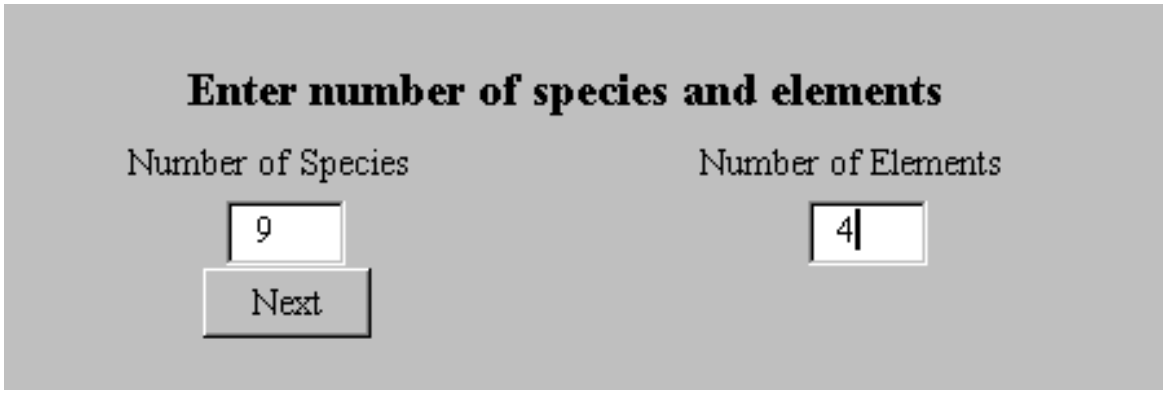

Figure 2: Window for entering number of species and elements

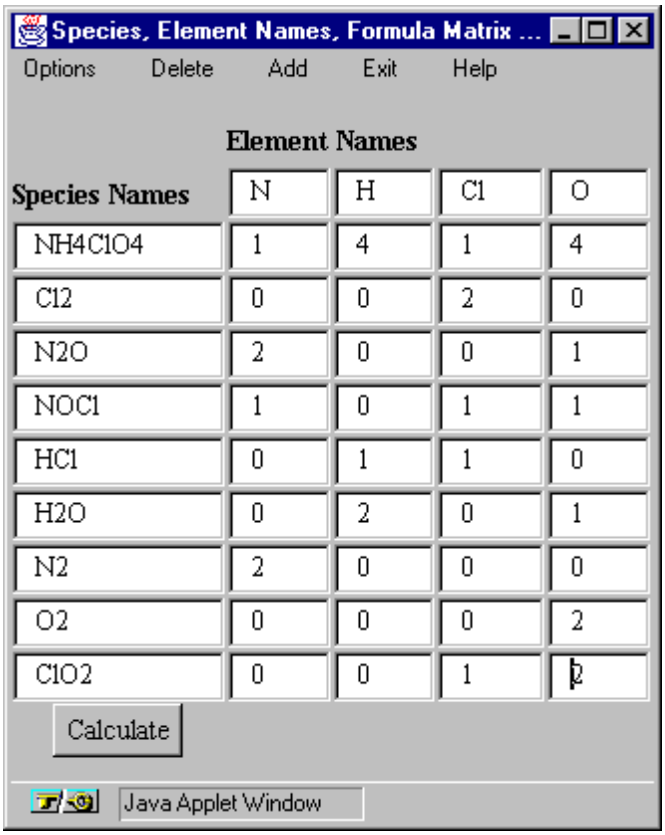

Figure 3: Window for entering species names and formulas

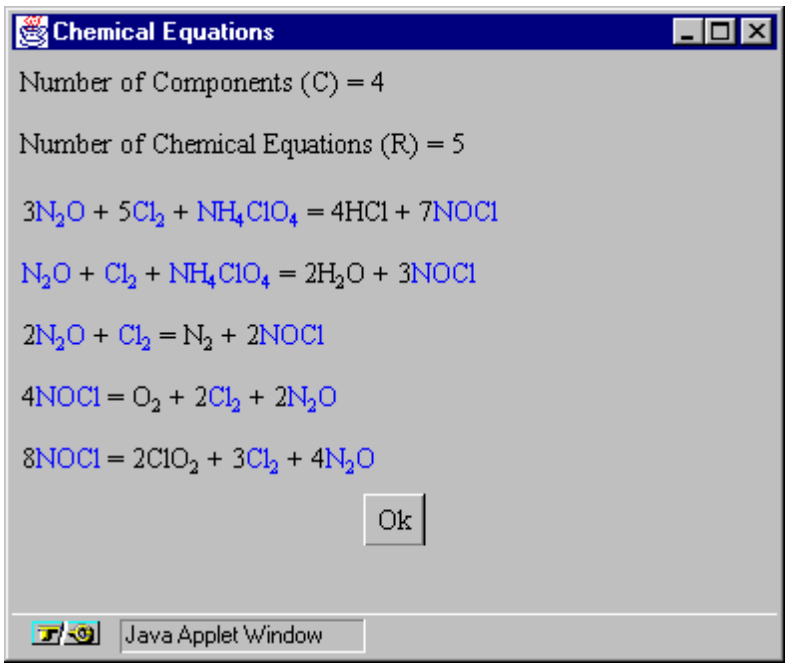

Figure 4: Window containing results of the calculation

6 Methodology

At about mid-March, 1998, information concerning the site was made available to a group of approximately ten interested individuals who acted as beta-testers. Based on their feedback, final changes were made prior to its official release at the end of March, 1998.

Following its release, our strategy for making the user community aware of the web site included registering it on search engines and making announcements on internet newsgroups, including sci.chem., sci.engr.chem, sci.edu, and sci.engr, as well as on several internet discussion groups.

On the site, we have included a mechanism for feedback, permitting the sending of an E-Mail message to the authors. Other feedback methods were also investigated.

7 Results and Discussion

The site was launched at the end of March, 1998. The site will be demonstrated and feedback obtained to date will be presented and discussed at the ASEE presentation.

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Nomenclature

Latin Letters

a_{ki}	subscript to element k in molecular formula of species i
$\mathbf{A}$	formula matrix: the $(M \times N)$ matrix whose entries are a_{ki}
$\mathbf{A}^*$	unit matrix or row-reduced echelon form of $\mathbf{A}$
C	number of component species; number of linearly independent atom-balance equations
CRS	chemical reaction stoichiometry
M	number of elements
MRM	matrix reduction method
N	number of species
p	(protonic) charge
R	maximum or proper number of linearly independent chemical equations

Subscripts

i, k	dummy indices

Other Symbols

=	denotes chemical equation
→	denotes (irreversible) chemical reaction

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