OXIDATION-REDUCTION CHEMICAL EQUATION BALANCING WITH MAPLE

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Abstract

In beginning chemistry classes, students are taught a variety of techniques for balancing chemical equations. The most common method is inspection. This paper addresses using a system of linear mathematical equations to solve for the stoichiometric coefficients. Many linear algebra books carry the standard balancing of chemical equations as an example of solving a system of linear equations. First, we present an example that we both use in our freshman algebra classes for modeling and problem solving and in our linear algebra class. Then we continue by giving a mathematical modeling algorithm for balancing the more complicated *oxidation-reduction (redox)* equations using a system of linear equations and solve using a computer-algebra system, Maple.

Introduction

During your life you have witnessed numerous chemical reactions. How would you describe them to someone else? How could you obtain quantitative information about what went on in the reaction? Chemists use stoichiometric chemical equations to answer these questions.

By definition a chemical equation is a written representation of a chemical reaction, showing the reactants and products, their physical states, and the direction in which the reaction proceeds. In addition, many chemical equations designate the conditions necessary (such as high temperature) for the reaction to occur. A chemical equation provides stoichiometric information about a chemical reaction, only if it is balanced.

For a chemical equation to be balanced, the same number of each kind of atom must be present on both sides of the chemical equation.

A chemical equation identifies the starting and finishing chemical as reactants and products: reactants → products

Example (combustion of propane)

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_20$$

A chemical equation is balanced when it reflects the conservation of matter. Conservation of matter states:

The Law of Conservation of Matter states that matter cannot be created or destroyed, only redistributed. In chemistry, it is represented by the fact that the sum of the masses of the reactants are equal to the sum of the products formed in a chemical reaction.

Chemical Equations Versus Mathematical Equations

We usually think of an equation like x+2x=3x as purely mathematical, even if x represents a physical quantity like distance or mass. A chemical equation may look like a mathematical equation, but it describes experimental observations: the quantities and kinds of reactants and products for a particular chemical reaction. Reactants appear on the left hand side of a chemical equation; products on the right. The products, which are the result of combining the reactants, are known from experimental observations -- they cannot be derived mathematically. In fact, combining the same reactants at different concentrations or temperatures often produces different products from the same reactants.

First-year chemistry students cannot predict these effects, and are not generally asked to predict these effects. On the other hand, a chemical equation is similar to a mathematical equation in that there are certain restrictions on what may appear on the left and right hand sides of a chemical reaction. These mathematical rules represent the effects of the conservation of matter on the reaction. The principle of the conservation of matter says that no atoms are destroyed or created during a chemical reaction.

How A Chemist Approaches Balancing An Equation

Many chemical equations, in the view of the chemists, can be balanced by inspection, that is, the process of "trial and error." The objectives of a chemist are as follows:

- recognize a balanced equation
- recognize an unbalanced equation
- balance by inspection chemical equations with given reactants and products
- write the unbalanced equation when given compound names for reactants and products

According to chemistry textbooks, here is a step-wise procedure to balance equations:

Step 1. Determine what reaction is occurring : know the reactants, the products, and the physical states.
Step 2. Write the unbalanced equation that summarizes the reaction described in Step 1.
Step 3. Balance the equation by inspection, start with the most complicated molecules. Do not change the identities of any reactant or product.

Thus, balancing the equation is done by inspection, a "trial and error" process that some students catch onto and some students do not.

Balancing Equations with Systems of Equations Using MAPLE

Many students are frustrated with the trial and error method and their inability to balance chemical equations. Balancing chemical equations can be an application of solving a linear system of equations. Placing variables as the multipliers for each compound and making equations for each type of atom results in a system of linear equations. This system is usually under-determined, meaning that there are more variables than equations. This leads to infinitely many solutions. Our goal is to provide a procedure to find one of these solutions in terms of integers. This method is best grasped through an example. It also lays the foundation for balancing the more complicated oxidation-reduction equations.

Example 1. We are presented with the following complicated unbalanced equation:

$$C_2H_8N_2(s) + N_2O_4(g) \rightarrow N_2(g) + CO_2(g) + H_2O(g)$$

This could be tough by inspection, so let's use a system of equations and a computer to help us solve the reduced-row echelon form.

The set up:
Step 1: Introduce five multipliers {*a*,*b*,*c*,*d*,*e*}

$$aC_2H_8N_2(s) + bN_2O_4(g) \rightarrow cN_2(g) + dCO_2(g) + eH_2O(g)$$

Step 2: Set up the following equations:

C: 2a = d
H: 8 a = 2 e
N: 2 a + 2b = 2c
O: 4 b = 2 d + e

Step 3:
C: 2a - d = 0
H: 8 a - 2 e = 0
N: 2 a + 2b - 2c = 0
O: 4 b - 2 d - e = 0

Put into matrix form:

Step 4:

$$\begin{bmatrix} 2 & 0 & 0 & -1 & 0 \\ 8 & 0 & 0 & 0 & -2 \\ 2 & 2 & -2 & 0 & 0 \\ 0 & 4 & 0 & -2 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \\ d \\ e \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Put into augmented matrix form:

Step 5:

$$[A \mid b] = \begin{bmatrix} 2 & 0 & 0 & -1 & 0 & 0 \\ 8 & 0 & 0 & 0 & -2 & 0 \\ 2 & 2 & -2 & 0 & 0 & 0 \\ 0 & 4 & 0 & -2 & -1 & 0 \end{bmatrix}$$

Step 6: Gaussian Elimination with Maple yields:

Chemical Balance with Maple

> **with(linalg):**

Warning, the protected names norm and trace have been redefined and unprotected

The set up of the matrix, **A**.

> **A:=linalg[matrix] (4,6,[2,0,0,-1,0,0,8,0,0,0,-2,0,2,2,-2,0,0,0,0,4,0,-2,-1,0]);**

$$A := \begin{bmatrix} 2 & 0 & 0 & -1 & 0 & 0 \\ 8 & 0 & 0 & 0 & -2 & 0 \\ 2 & 2 & -2 & 0 & 0 & 0 \\ 0 & 4 & 0 & -2 & -1 & 0 \end{bmatrix}$$

We now need the reduced row echelon form of the matrix A.

➢ **gaussjord(A,'r');**

$$\begin{bmatrix} 1 & 0 & 0 & 0 & \frac{-1}{4} & 0 \\ 0 & 1 & 0 & 0 & \frac{-1}{2} & 0 \\ 0 & 0 & 1 & 0 & \frac{-3}{4} & 0 \\ 0 & 0 & 0 & 1 & \frac{-1}{2} & 0 \end{bmatrix}$$

$$[A] = \begin{bmatrix} 1 & 0 & 0 & 0 & -1/4 & 0 \\ 0 & 1 & 0 & 0 & -1/2 & 0 \\ 0 & 0 & 1 & 0 & -3/4 & 0 \\ 0 & 0 & 0 & 1 & -1/2 & 0 \end{bmatrix}$$

Simplify (by chemistry rules of lowest integer solution).

Step 7: Choose e =4

a=1/4 e , so a=1
b=1/2 e so b =2
c= 3/4 e, so c =3
d = 1/2 e, so d =2

Balance the equation

Step 8:

$1C_2H_8N_2(s) + 2N_2O_4(g) \rightarrow 3N_2(g) + 2CO_2(g) + 4H_2O(g)$

Check:
C: 2=2
H: 8 = 8
N: 2 + 4 = 6, 6=6
O: 8 = 4 + 4, 8 =8

The equation checks and is balanced.

Balancing the More Complicated Oxidation-Reduction Equations (Redox reactions) By a Chemist

These equations are the more difficult to balance. The chemistry books suggest a methodology that also involves "inspection". There are two types of oxidation-reduction equations: acidic and basic solutions.

The steps in Oxidation-Reduction Reactions in Acidic Solution via standard chemistry textbooks are as follows:

Step 1. Write separate equations for oxidation and reduction half-reactions.
Step 2. For each equation: (a) Balance all elements except hydrogen and oxygen (b) Balance oxygen using H_20 (c) Balance hydrogen using H^+ (d) Balance the charge. Thus, in acidic solution, we balance H and O atoms with H_20 and charge with H^+.
Step 3. If necessary multiply balanced equations by integers to equalize electrons.
Step 4. Add the half-reaction and cancel identical species
Step 5. Check that the elements and charges are balanced

The steps in Oxidation-Reduction Reactions in Basic Solution from a standard chemistry textbook are as follows:

Step 1. Use the half-reaction method as previously specified for acidic solutions to obtain a balanced equation *as if H^+ ions were present*.
Step 2. To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. In basic solution, H_20 balances H and O atoms and OH^- balances the charge.
Step 3. Form H_20 on the side containing both H^+ and OH^- ions, and eliminate the number of H_20 molecules that appear on both sides.
Step 4. Check that the elements and charges are balanced.

Balancing Equations with the Conservation of Mass and Charge, *Oxidation-Reduction Equations,* with Systems of Equations with Maple

Step 1: Apply appropriate variables for either acidic or basic solutions

For Acid:

$$(\text{Reactants}) + H^+ \longrightarrow (\text{Products}) + H_2O$$

For Base

$$(\text{Reactants}) + H_2O \longrightarrow (\text{Products}) + OH^-$$

Step 2 Create equations that balance atoms
Step 3 Create charge conservation equation
Step 4 Place into augmented coefficient matrix
Step 5 Use Gaussian elimination (Use a Reduced Row Echelon Form)
Step 6 Select the value of the free variables to create integer solutions
Step 7 Write the balanced equation

Step #3 requires the student to model a new equation for the oxidation-reduction reaction using oxidation numbers. An atom's oxidation number signifies the number of charges the atom would have in a molecule if all electrons were completely transferred. We will use the following rules to assign oxidation numbers:

1. In free elements, each atom has an oxidation number of zero. Thus each atom, in a stand alone reaction (such as Na, H_2, Br, K, and S_4) have the same oxidation number, zero.
2. The oxidation number of a monotonic ion is the same as the charge. For example, the oxidation number of Na^+ ion is +1 and of Cl^- ion is –1.
3. In compounds, fluorine is always assigned an oxidation number of –1.
4. Oxygen is always assigned an oxidation number of –2 in its compounds.
5. In compounds with nonmetals, hydrogen is assigned an oxidation number of +1.

6. The sum of the oxidation states **must** equal zero for an electronically neutral compound.

We illustrate these rules to obtain the oxidation equation in the following examples.

Example 2. Consider the following redox equation with elements copper (Cu), hydrogen (H), nitrogen (N), and oxygen (O).

$$Cu + HNO_{3(aq)} \longrightarrow Cu_{(aq)}{}^{2+} + NO_{2(g)} + NO_{3(aq)}{}^{1-} + H_2O_{(l)}$$

If we add our multipliers, we have six unknowns and only four chemical elements:

$$x_1Cu + x_2HNO_3 \longrightarrow x_3Cu^{2+} + x_4NO_2 + x_5NO_3{}^{1-} + x_6H_2O$$

Copper:	$x_1=x_3$
Hydrogen:	$x_2=2x_6$
Nitrogen:	$x_2=x_4+x_5$
Oxygen:	$3x_2= 2\,x_4+3x_5+x_6$

It might appear as though we cannot use the system of equations method because of the six equations and only four elements. However, charge must be conserved as well, giving rise to another equation. We list the charges with each element. These are the oxidation numbers. They are found in the tables of chemistry textbooks.

$$\overset{+0}{Cu} + \overset{+1}{H}\,\overset{+5}{N}\,\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}{}^{2+} + \overset{+2}{N}\,\overset{-2}{O} + \overset{+5}{N}\,\overset{-2}{O_3}{}^{1-} + \overset{+1}{H_2}\,\overset{-2}{O}$$

and with our set of multipliers

$$x_1\overset{+0}{Cu} + x_2\,\overset{+1}{H}\,\overset{+5}{N}\,\overset{-2}{O_3}$$

$$\longrightarrow$$

$$x_3\,\overset{+2}{Cu}{}^{2+} + x_4\,\overset{+2}{N}\,\overset{-2}{O} + x_5\,\overset{+5}{N}\,\overset{-2}{O_3}{}^{1-} + x_6\,\overset{+1}{H_2}\,\overset{-2}{O}$$

This generates the following equation

$$x_1 \cdot 0 + x_2 \cdot 5 = x_3 \cdot 2 + x_4 \cdot 2 + x_5 \cdot 5 + x_6 \cdot 0$$

Notice that this equation using only oxidation numbers of atoms whose oxidation numbers are changing.

The equation may be rewritten as:

$$0x_1 + 5x_2 - 2x_3 - 2x_4 - 5x_5 - 0x_6 = 0$$

We put all the equations in a augmented matrix form:

$$\begin{bmatrix} 1 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -2 & 0 \\ 0 & 1 & 0 & -1 & -1 & 0 & 0 \\ 0 & 3 & 0 & -2 & -3 & -1 & 0 \\ 0 & 5 & -2 & -2 & -5 & 0 & 0 \end{bmatrix}$$

The solution with Maple yields the following:

Chemical Balancing with Oxidation-Reduction

```
> A:=linalg[matrix] (5,7,[1,0,1,0,0,0,0,0,1,
0,0,0, -2,0,0,1,0,-1,-1,0,0,0,3,0,-2,-3,-1,0,0,5,-2,
-2,-5,0,0]);
```

$$A := \begin{bmatrix} 1 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -2 & 0 \\ 0 & 1 & 0 & -1 & -1 & 0 & 0 \\ 0 & 3 & 0 & -2 & -3 & -1 & 0 \\ 0 & 5 & -2 & -2 & -5 & 0 & 0 \end{bmatrix}$$

We now need the reduced row echelon form of the matrix A.

```
> gaussjord(A,'r');
```

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & \frac{-3}{2} & 0 \\ 0 & 1 & 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 1 & 0 & 0 & \frac{-3}{2} & 0 \\ 0 & 0 & 0 & 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 \end{bmatrix}$$

>

We note that the commands in Maple are the same as the previous example. The key component here is the modeling of Step #3 that produces the required additional equation needed to properly balance the oxidation-reduction equation.

We obtain the solution with a free variable.

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{bmatrix} = x_6 \begin{bmatrix} \frac{3}{2} \\ 2 \\ \frac{3}{2} \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

We choose the solution to the free variable to be the smallest integer value that clears all fractions. Thus, we choose to let $x_6=2$, thus obtaining the following

$$x_1 = 3$$
$$x_2 = 4$$
$$x_3 = 3$$
$$x_4 = 2$$
$$x_5 = 2$$
$$x_6 = 2$$

We write the balanced form as

$$3\overset{+0}{Cu} + 4\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 \longrightarrow 3\overset{+2}{Cu}^{2+} + 2\overset{+2}{N}\overset{-2}{O} + 2\overset{+5}{N}\overset{-2}{O}_3{}^{1-} + 2\overset{+1}{H}_2\overset{-2}{O}$$

We check our balanced equation.

	Left Side	Right Side
Cu	3	3
H	4	4
N	4	4
O	12	12

We also check to see that the electrons balance:

Electrons:	20	20

Since 20=20, our electrons balance.
Thus, we have a balanced equation.

Example 3. Consider the following unbalanced oxidation-reduction reaction

$CH_3CH_2OH+Cr2O^{2-}{}_7+H^+ \rightarrow CH_3CO_2H+Cr^{3+}+H_2O$

Obtain the oxidation numbers and we model only those elements whose oxidation numbers actually change:

-3 +1 –1 +1 –2 +1 +6 –2 2- +1 -3 +1 +3 –2 –2 +1 +3
$CH_3CH_2OH+Cr_2O_7+H^+ \rightarrow CH_3CO_2H+Cr^{3+}+$
+1 -2
H_2O

We look at what oxidation levels change and build an appropriate equation:

$$\overset{-1}{C} \rightarrow \overset{+3}{C}$$
$$\overset{+6}{Cr} \rightarrow \overset{+3}{Cr}$$

We obtain the oxidation equation as
$-x_1+12x_2+0x_3-3x_4-3x_5+0x_6=0$

Carbon:	$2x_1-2x_4=0$
Hydrogen:	$6x_1+x_3-4x_4-2x_6=0$
Chromium:	$2x_2-x_5=0$
Oxygen:	$1x_1+7x_2-2x_3-x_6=0$
Oxidation:	$-x_1+12x_2+0x_3-3x_4-3x_5+0x_6=0$

We put into matrix form in Maple and then solve

$$A := \begin{bmatrix} 2 & 0 & 0 & -2 & 0 & 0 & 0 \\ 6 & 0 & 1 & -4 & 0 & -2 & 0 \\ 1 & 7 & 0 & -2 & 0 & -1 & 0 \\ 0 & 2 & 0 & 0 & -1 & 0 & 0 \\ -1 & 12 & 0 & -3 & -3 & 0 & 0 \end{bmatrix}$$

We use Maple to obtain:

$$B := \left[\begin{array}{cccccc|c} 1 & 0 & 0 & 0 & 0 & \frac{-3}{11} & 0 \\ 0 & 1 & 0 & 0 & 0 & \frac{-2}{11} & 0 \\ 0 & 0 & 1 & 0 & 0 & \frac{-16}{11} & 0 \\ 0 & 0 & 0 & 1 & 0 & \frac{-3}{11} & 0 \\ 0 & 0 & 0 & 0 & 1 & \frac{-4}{11} & 0 \end{array}\right]$$

We allow the free variable, $x_6 = 11$, to clear the fractions at the lowest value. This makes $x_1=3$, $x_2=2$, $x_3=16$, $x_4=3$, $x_5=4$, and $x_6=11$. Our balanced equationis:

$3(CH_3CH_2OH)+2(Cr_2O^{2-}_7+)16H^+ \rightarrow$
$3(CH_3CO_2H)+4Cr^{3+}+11(H_2O)$

Checking the balancing:

Carbon: 6 = 6
Hydrogen: 34= 34
Oxygen: 17 =17
Chromium: 4=4
Electrons: 21=21

We have balanced our oxidation-reduction equation.

Summary and Conclusions

Oxidation-reduction, *redox* equations, involves acidic or basic solution in their reactions reactions. These need to be recognized by your knowledge of chemistry and use the following prior to starting the balancing procedure.

For Acid:

$$(\text{Reactants}) + H^+ \longrightarrow (\text{Products}) + H_2O$$

For Base

$$(\text{Reactants}) + H_2O \longrightarrow (\text{Products}) + OH^-$$

In summary, for the more complicated oxidation-reduction equations involving conservation of mass and/or charge, we apply the following steps in order to accurately balance the equation.

- Apply variables
- Create equations that balance atoms
- Create charge conservation equation
- Place into augmented coefficient matrix
- Use Gaussian elimination (Use a Reduced Row Echelon Form)
- Select the value of the free variables to create integer solutions
- Write and check the balanced equation

Once the equations are established the use of technology such as Maple can generate a reduced row echelon solution.

We have found that the students enjoy learning the basic balancing of chemical equations in our freshman college algebra classes as an example of solving systems of equations. The students enjoy the aspects of building the equation models, solving the system of equations, and putting the result back into chemistry language and symbols. In our linear algebra classes, our students are exposed to these same techniques but requiring more analysis of the concepts Of linear algebra. The oxidation-reduction methodology, using the linear algebra concepts, provides an easier mathematical algorithm to obtain the solution than the methodology that is currently taught in chemistry courses. It is our goal to have these mathematical methods appear in the modern chemistry textbooks.

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Biographical Information

Dr. William P. Fox received his B.S. Degree from the United States military Academy at West Point, New York, his M.S. at the Naval Postgraduate School, and his Ph.D. at Clemson University. He has taught mathematics at USMA, Francis Marion University, and currently is a Professor and is teaching mathematical modeling at the Naval Postgraduate School. He serves as the associate contest director for COMAP's Collegiate Mathematical Contest in Modeling (MCM) and serves as contest director for the High School Mathematical Contest in Modeling (HiMCM). His interests include applied mathematics, mathematical modeling, optimization (linear and nonlinear), statistical models for medical research, and computer simulations.

Dr. Kris Varazo is currently as Assistant Professor of Chemistry at Francis Marion University. He teaches general chemistry and the analytical chemistry courses. His research interests are in chemical education and nanotechnology. He obtained a B.S. degree in Chemistry and Biochemistry from the University of West Florida and a Ph.D. from the University of Georgia under the direction of John Stickney. He also worked with Donna A. Chen as a Postdoctoral Fellow at the University of South Carolina.

Joshua Croteau, a senior, is an honor student at Francis Marion University majoring in mathematics with a minor in creative writing. He is a member of Kappa Mu Epsilon mathematics honor society.