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ABSTRACT

This material was developed to provide an application of matrix mathematics in chemistry, and to show the concepts of linear independence and dependence in vector spaces of dimensions greater than three in a concrete setting. The techniques presented are not intended to be considered as replacements for such chemical methods as oxidation-reduction or the balancing of half-reactions. It is noted that it is possible to write down a chemical reaction that does not take place and still balance it by the matrix methods provided. Exercises and references are included to the problems supplied. (MP)

umap

UNIT 339

MODULES AND MONOGRAPHS IN UNDERGRADUATE MATHEMATICS AND ITS APPLICATIONS PROJECT

BALANCING CHEMICAL REACTIONS WITH MATRIX METHODS AND COMPUTER ASSISTANCE

by Ralph P. Grimaldi

$C + HNO_3 \rightarrow NO_2 + H_2O + CO_2$

$H_2O_2 + NaMnO_4 + HC\ell \rightarrow MnC\ell_2 + H_2O + O_2 + NaC\ell$

$KCN + KMnO_4 \rightarrow KCNO + MnO_2$

$KC\ell O_3 + C_{12}H_{22}O_{11} \rightarrow CO_2 + H_2O + KC\ell$

APPLICATIONS OF LINEAR ALGEBRA TO CHEMISTRY

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BALANCING CHEMICAL REACTIONS WITH MATRIX METHODS AND COMPUTER ASSISTANCE

by

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TABLE OF CONTENTS

Intermodular Description Sheet: UMAP Unit 339

Title: BALANCING CHEMICAL REACTIONS WITH MATRIX METHODS AND COMPUTER ASSISTANCE

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Classification: APPL LIN ALG/CHEM

Prerequisite Skills:

1. Elementary matrix operations including the inverting of square matrices.
2. Some introductory chemistry on nomenclature and balancing chemistry equations.
3. Some knowledge of BASIC or BASIC PLUS would make comprehension of the module complete but is not totally necessary and depends on the individual instructor's intentions for the module's use.

Output Skills:

1. To reinforce the abstract concept of linear independence by appealing to a concrete setting where the dimension exceeds 3.
2. To apply the inverse matrix method for solving linear systems to situations arising from chemical reactions.

MODULES AND MONOGRAPHS IN UNDERGRADUATE MATHEMATICS AND ITS APPLICATIONS PROJECT (UMAP)

The goal of UMAP is to develop, through a community of users and developers, a system of instructional modules in undergraduate mathematics and its applications which may be used to supplement existing courses and from which complete courses may eventually be built.

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1. INTRODUCTION

This module was developed to provide an application of matrix mathematics in chemistry, and to show the concepts of linear independence and dependence in vector spaces of dimension greater than 3 in a concrete setting.

In balancing a chemical reaction such as

$$Pb(N_3)_2 + Cr(MnO_4)_2 \to Cr_2O_3 + MnO_2 + Pb_3O_4 + NO$$

we seek positive integers u,v,w,x,y,z, which have no common divisor other than 1, so that

$$(u)Pb(N_3)_2 + (v)Cr(MnO_4)_2 \to (w)Cr_2O_3 + (x)MnO_2 + (y)Pb_3O_4 + (z)NO.$$

We say that the equation or reaction is *balanced* when the number of atoms of each chemical element involved is the same on each side of the reaction. For example, here, for the element Pb (lead), there are u atoms on the left side (the *reactant side*) of the reaction, and 3y atoms of Pb on the right side (the *product side*). The 3 in the term 3y comes from the fact that there are 3 atoms of Pb in each Pb_3O_4 molecule. For the reaction to be balanced we must have u = 3y. In the same way we count the respective number of atoms on both sides of the reaction for the other chemical elements N, Cr, Mn, and O, and obtain a linear system of equations. The setting up of this system and its solution by matrix methods will be examined in detail in Section 4.1.

2. BACKGROUND: MATHEMATICAL AND CHEMICAL

2.1 Vectors in Two and Three Dimensions

Consider the operations of vector addition and scalar multiplication in the Euclidean plane, R^2, where $(x,y) + (x',y') = (x + x', y + y')$ and $r(x,y) = (rx,ry)$ for any $(x,y),(x',y') \in R^2$, $r \in R$. Starting with the

vector $\vec{i} = (1,0)$, and using only these operations, we can "build" or "construct" any vector in R^2 of the form $(r,0)$, $r \in R$. However, to generate every vector (x,y) in R^2 we need an additional vector such as $\vec{j} = (0,1)$, which is not a scalar multiple of $\vec{i}$. We cannot construct any vector with nonzero second component by applying our given operations only to $\vec{i} = (1,0)$. For instance, it is impossible to express the vector $\vec{j} = (0,1)$ as a sum of scalar multiples of $\vec{i} = (1,0)$.

In like manner, starting with the vectors $\vec{i} = (1,0,0)$ and $\vec{j} = (0,1,0)$ in Euclidean space, R^3, and using the standard operations of vector addition and scalar multiplication in R^3, as we did in R^2, we can form any vector in the xy-plane, that is, all vectors whose third component is 0. However, once again, to be able to construct every vector (x,y,z) of R^3 we need an additional vector whose third component is not zero. With $\vec{k} = (0,0,1)$, and $\vec{i}$ and $\vec{j}$ as above, we can form any vector in Euclidean space using vector addition and scalar multiplication. We could not have done this with just $\vec{i}$ and $\vec{j}$, for it is impossible to "decompose" the vector $\vec{k}$ into a linear combination, $r_1\vec{i} + r_2\vec{j}$, of the vectors $\vec{i}$ and $\vec{j}$, with r_1 and $r_2 \in R$. We might also say that the vector $\vec{k}$ is not dependent upon $\vec{i}$ and $\vec{j}$ or that the vectors $\vec{i}, \vec{j}$ and $\vec{k}$ are linearly independent.

2.2 A Word About Chemical Elements

In this section we shall see that the word "decompose" which appears in the last paragraph of Section 2.1 was specifically chosen for its suggestive value.

In the science of chemistry the term *pure substance* is used to describe any variety of matter which has a recognizably definite composition and possesses specific properties. The chemical reaction of *decomposition* is one in which such a pure substance breaks down to yield simpler forms of matter. Many of the substances known to scientists do this, and release or absorb as much energy as 30,000 calories per gram in the process. (Processes that involve changes in the nucleus of a chemical element may result in even higher energy changes. This kind of reaction is termed *nuclear* rather than chemical.) Among all such pure substances, those that do not break down at all within the energy range mentioned, or that give only one final product, as in the decomposition of ozone into oxygen, are called the *elements*. As of 1970 there were 105 known elements. (Element 105, Hahnium, chemically denoted Ha, was discovered in that year by the team of Ghiorso, Nurmia, Harris, K.A.Y. Eskola, and P.L. Eskola.) Elements are considered to be the chemical building blocks for forming all other substances; the smallest chemical unit of any such element being called an *atom*.

3. SOLVING LINEAR SYSTEMS: THE INVERSE MATRIX METHOD

One of the main topics covered in a first course in matrix algebra is the solution of a system of linear equations by way of techniques such as elementary row operations, Cramer's rule or the inverse matrix method. We shall find the inverse matrix method most suitable for our applications in Section 4.

The method can be described as follows: given a system of linear equations such as

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = b_1 ;$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = b_2 ,$$

$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 = b_3 ;$$

we can write this system in matrix form as

$$AX = B, \text{ where } A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}, \; X = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \; B = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}$$

In elementary algebra, if a and b are real numbers, and $a \neq 0$, then the solution of the equation

$$ax = b$$

is

$$x = a^{-1}b.$$

We would like to expand this idea to the matrix equation $AX = B$, where A,B are matrices of real numbers, and be able to conclude that the solution is $X = A^{-1}B$. Here, however, we need more than just $A \neq 0$. We need $\det A \neq 0$, where det A is the determinant of the matrix A. One finds this to happen when the linear system is *independent*, that is, when none of the equations in the system can be obtained by combining multiples of some of the other equations.

4. BALANCING CHEMICAL REACTIONS

4.1 The Computer Supplies a Readily Recognizable Answer

Our first problem reads as follows: The reaction of lead (II) azide and chromium (II) permanganate in producing chromium (III) oxide, manganese (IV) dioxide, trilead tetroxide, and nitric oxide is given by the chemical equation

(1) $Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2 + Pb_3O_4 + NO$ (basic solution),

a reaction involving 3 oxidations and 1 reduction.

Before we tackle the problem of trying to balance this equation, let us reconsider the idea of linear independence of vectors in a chemical setting. Just as we could not create the vector $\vec{k} = (0,0,1)$ from the vectors $\vec{i} = (1,0,0)$, $\vec{j} = (0,1,0)$ in Section 2.1, in dealing with the above chemical equation, we know for instance, that we cannot create Pb from N and O or any other combination of elements from among N, O, Cr, Mn. This is inherent in the very nature of a chemical element, and we may thus view the elements involved in the chemical reaction as independent vectors in R^5. We shall make the following atom assignments in solving the problem:

$$Pb = (1,0,0,0,0), \quad Mn = (0,0,0,1,0),$$
$$N = (0,1,0,0,0), \quad O = (0,0,0,0,1).$$
$$Cr = (0,0,1,0,0),$$

The basis for this idea can be found on pp. 26-27 of [2].

To balance the equation,

(2) $$Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2 + Pb_3O_4 + NO$$

(basic solution),

we must find integers u,v,w,x,y,z, with no common integer divisors other than ± 1, so that

(3) $$(u)Pb(N_3)_2 + (v)Cr(MnO_4)_2 \rightarrow (w)Cr_2O_3 + (x)MnO_2 + (y)Pb_3O_4 + (z)NO.$$

Using the vector assignments above, we replace the chemical equation (3) by the vector equation

(4) $$u(1,6,0,0,0) + v(0,0,1,2,8) = w(0,0,2,0,3) + x(0,0,0,1,2) + y(3,0,0,0,4) + z(0,1,0,0,1),$$

where, for example, (1,6,0,0,0) represents the lead (II) azide molecule, $Pb(N_3)_2$, since it is made up of 1 atom of Pb and 6 atoms of N, and using vector addition and scalar multiplication $(1,6,0,0,0) = 1(1,0,0,0,0) + 6(0,1,0,0,0)$.

Since vectors are equal only when all corresponding components are equal, by equating the first through fifth components in equation (4) we get the following system of 5 equations in 6 unknowns,

(5)
$$\begin{aligned} u + 0v &= 0w + 0x + 3y + 0z \\ 6u + 0v &= 0w + 0x + 0y + z \\ 0u + v &= 2w + 0x + 0y + 0z \\ 0u + 2v &= 0w + x + 0y + 0z \\ 0u + 8v &= 3w + 2x + 4y + z \end{aligned}$$

or,

(6)
$$\begin{aligned} 0v + 0w + 0x + 3y + 0z &= u \\ 0v + 0w + 0x + 0y + z &= 6u \\ -v + 2w + 0x + 0y + 0z &= 0u \\ -2v + 0w + x + 0y + 0z &= 0u \\ -8v + 3w + 2x + 4y + z &= 0u \end{aligned}$$

There are infinitely many solutions of this system. But from a chemical viewpoint this is in keeping with our experience, for if we have one solution that balances the chemical equation (3), any positive integer multiple of it yields another solution. Also, before proceeding, it should be pointed out that the techniques developed here work for our chemical reactions because they are electrically balanced.

Since we are not interested in the general solution, let us find the unique solution corresponding to $u = 1$. In matrix notation this will take the following form

(7) $$\begin{bmatrix} 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ -1 & 2 & 0 & 0 & 0 \\ -2 & 0 & 1 & 0 & 0 \\ -8 & 3 & 2 & 4 & 1 \end{bmatrix} \begin{bmatrix} v \\ w \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 \\ 6 \\ 0 \\ 0 \\ 0 \end{bmatrix},$$

so that

$$(8)\quad \begin{bmatrix} v \\ w \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ -1 & 2 & 0 & 0 & 0 \\ -2 & 0 & 1 & 0 & 0 \\ -8 & 3 & 2 & 4 & 1 \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 6 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

The solution is immediate once we get the inverse of the given 5 × 5 matrix. Now although one can find an inverse for a square matrix A, where det A ≠ 0, by such methods as elementary row operations as found in Chapter 1 of [1], or by use of the adjoint as described in Chapter 2 of [1], it is at this point that we shall use some computer assistance via the following BASIC-PLUS program:

```
10 REM THIS PROGRAM IS USED IN BALANCING CHEMICAL EQUATIONS
20 DIM A(5,5),B(5,1),I(5,5),S(5,1)
30 MAT READ A,B
40 MAT I = INV(A)
50 MAT S = I*B
60 DATA 0,0,0,3,0
70 DATA 0,0,0,0,1
80 DATA -1,2,0,0,0
90 DATA -2,0,1,0,0
100 DATA -8,3,2,4,1
110 DATA 1,6,0,0,0
120 PRINT "V=";S(1,1),"W=";S(2,1),"X=";S(3,1),"Y=";S(4,1),
    "Z=";S(5,1)
130 STOP
140 INPUT "K = "; K
150 DIM T(5,1)
160 MAT T = (K)*S
170 PRINT "U=";K,"V=";T(1,1),"W=";T(2,1),"X=";T(3,1),
    "Y=";T(4,1)
180 PRINT "Z=";T(5,1)
190 END

Ready

RUNNH
V= 2.93333   W= 1.46667   X= 5.86667   Y= .333333   Z= 6
Stop at line 130

Ready
```


This program uses matrix operations that are available in BASIC or BASIC-PLUS. An excellent explanation of these computer matrix operations can be found in Chapter 10 of [4]. (The program here and all others found in this module were run at the Rose-Hulman Institute of Technology on a DEC PDP 11/70 using the RSTS version 7 operating system.)

At this point we must be prepared to recognize 0.03333 as 1/30 and 0.06667 as 2/30. So to express the answers in integer form we shall perform the scalar multiplication at line 160 by inputing the value of K at line 140 as 30, the least common denominator for all fractions involved. Upon typing CONT we get the following output.

```
CONT
K = ? 30
U= 30     V= 88     W= 44     X= 176     Y= 10
Z= 180

Ready
```

Dividing each coefficient by 2 we find the equation balanced as follows:

$$(9)\quad 15\ Pb(N_3)_2 + 44\ Cr(MnO_4)_2 \rightarrow 22\ Cr_2O_3 + 88\ MnO_2 + 5\ Pb_3O_4 + 90\ NO.$$

In some balancing problems, it is possible to reduce the number of independent vectors involved if we can find a radical that does not break down in the reaction. The CN in the reaction

$$KCN + KMnO_4 \rightarrow KCNO + MnO_2$$

is a case in point. Instead of assigning a 5-dimensional vector to each of K, C, N, Mn, and O to balance this equation, we may assign a 4-dimensional vector to each of K, CN, Mn, and O. This simplifies the problem.

4.2 The Computer Supplies an Answer Which Is Not Easily Recognized

If we compare the 5 × 5 coefficient matrix in Equation (7) with the equations in (6), we see that the columns of the matrix are the vector representations of the molecules other than the first reactant. The minus signs occur in the columns for the other reactants. The product molecules have all positive components in their respective columns. The 5 × 1 column matrix of constants in (7) results from the vector representation of the first reactant, $Pb(N_3)_2$.

We shall now consider a second problem which will give us an opportunity to extend our use of matrix operations in BASIC-PLUS to the MAT INPUT statement and will employ the transpose of a matrix. This particular problem will provide us with techniques to consider when the output does not yield decimals whose equivalent fractions are as obvious as in the first problem we considered. In addition, the program below is more general and can be used in balancing other electrically balanced chemical equations.

Here we shall consider the chemical reaction

(10) $$H_2SO_4 + MnS + As_2(Cr_2O_7)_5 \rightarrow HMnO_4 + AsH_3 + Cr_2(SO_4)_3 + H_2O\ .$$

(This involves 2 oxidations and 2 reductions.)

We assign the following vectors to the atoms:

$$H = (1,0,0,0,0,0),\quad Mn = (0,0,0,1,0,0),$$
$$S = (0,1,0,0,0,0),\quad As = (0,0,0,0,1,0),$$
$$O = (0,0,1,0,0,0),\quad Cr = (0,0,0,0,0,1)\ .$$

To balance the chemical reaction (10) we need to find integers t,u,v,w,x,y,z, as in Section 4.1, so that

(11) $$t(2,1,4,0,0,0) + u(0,1,0,1,0,0) + v(0,0,35,0,2,10) = w(1,0,4,1,0,0) + x(3,0,0,0,1,0) + y(0,3,12,0,0,2) + z(2,0,1,0,0,0)\ .$$

Letting t = 1, we can write the vector equation (11) in the equivalent matrix form AX = B:

(12) $$\begin{bmatrix} 0 & 0 & 1 & 3 & 0 & 2 \\ -1 & 0 & 0 & 0 & 3 & 0 \\ 0 & -35 & 4 & 0 & 12 & 1 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 & 0 \\ 0 & -10 & 0 & 0 & 2 & 0 \end{bmatrix} \cdot \begin{bmatrix} u \\ v \\ w \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 2 \\ 1 \\ 4 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

Accordingly, the solution for the vector equation when t = 1 is given by

(13) $$\begin{bmatrix} u \\ v \\ w \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 3 & 0 & 2 \\ -1 & 0 & 0 & 0 & 3 & 0 \\ 0 & -35 & 4 & 0 & 12 & 1 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 & 0 \\ 0 & -10 & 0 & 0 & 2 & 0 \end{bmatrix}^{-1} \begin{bmatrix} 2 \\ 1 \\ 4 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

Once again we shall turn to the computer for assistance in solving the matrix equation. Here, however, our program is somewhat different from that used in Section 4.1. It involves the transpose of a matrix, that is, the matrix that results from a given matrix by interchanging its rows and columns. (For more on the transpose of a matrix see pp. 67-68 of [1].)

```
10 REM THIS PROGRAM IS USED IN BALANCING CHEMICAL REACTIONS
20 REM N IS THE NUMBER OF DISTINCT ATOMS OR RADICALS INVOLVED
30 DIM A(20,20), B(20,1), I(20,20), J(20,20), S(20,1)
40 INPUT "N ="; N
50 MAT INPUT A(N,N)
60 MAT INPUT B(N,1)
70 MAT I = TRN(A)
80 MAT J = INV(I)
90 MAT S = J*B
100 MAT PRINT S
110 END

Ready
```

At line 50 of this program we input the columns of the 6 × 6 matrix A of Equation (12). We start with (0,-1,0,-1,0,0), the negative of the vector representation of the second reactant MnS, and continue until we finish with the vector (2,0,1,0,0,0) for the last product H_2O. At line 60 we input the vector representation, (2,1,4,0,0,0), of the reactant H_2SO_4. (The input is provided at the keyboard like the usual INPUT statement. A question mark appears when the computer is ready to receive the data. Upon typing in the value of N and hitting the RETURN key, the line feed key can be used if we wish to type the vector representations on successive lines, as shown in the rows following the inputting of the value of N. We then hit RETURN after typing in the last row vector.)

Lines 30, 40, 50, 60 constitute a redimensioning of the original matrices A and B. This allows the program to be flexible in its application to any electrically balanced equation that involves 20 or fewer atoms or radicals.

Upon typing RUNNH and inputting the value of N and the vector components for the reactants and products, the program yields the following results:


```
RUNNH
N =? 6
? 0,-1,0,-1,0,0
? 0,0,-35,0,-2,-10
? 1,0,4,1,0,0
? 3,0,0,0,1,0
? 0,3,12,0,0,2
? 2,0,1,0,0,0
? 2,1,4,0,0,0
 .308725
 .872483E-1
 .308725
 .174497
 .436242
 .583893

Ready
```

From the printout here we see that for $t = 1$, we obtain $u = .308725$, $v = .0872483$, $w = .308725$, $x = .174497$, $y = .436242$, $z = .583893$, which unfortunately are not readily recognizable as any specific "easy" fractions. However, if we divide each variable by the smallest value, namely .0872483 (since in chemical reactions we are primarily concerned with the ratios of compounds), we get a second solution where

$$t = 11.46154, \quad x = 2.00000,$$
$$u = w = 3.53846, \quad y = 5.00000,$$
$$v = 1, \quad z = 6.69231,$$

to *five decimal places*.

Now considering all the fractional parts, we find that $0.53846 - 0.46154 = 0.07692$ is the smallest difference and that $(0.07692)^{-1} = 13.00052$, so $0.07692 \doteq 1/13$. Then $0.46154 \doteq 6/13$, and $0.69231 \doteq 9/13$.

So multiplying our solution through by 13, we find the reaction balanced as follows:

(14) $$149\ H_2SO_4 + 46\ MnS + 13\ AS_2(Cr_2O_7)_5 \rightarrow 46\ HMnO_4 + 26\ AsH_3 + 65\ Cr_2(SO_4) + 87\ H_2O.$$

4.3 Have We Only Dealt With Very Special Cases?

You may have noticed in reading Sections 4.1 and 4.2 that, to set up the matrix equations used there, both chemical reactions discussed were of the type where the total number of reactants and products exceeded the number of atoms and radicals involved by exactly 1. The number n of radicals and atoms controls the number of linear equations involved, while the number m of reactants and products controls the number of unknowns. One need not look very far to find a chemical reaction where $n \neq m + 1$. In this section we shall deal with the case where $n = m$.

To balance the chemical reaction,

(15) $$KC\ell O_3 + C_{12}H_{22}O_{11} \rightarrow CO_2 + H_2O + KC\ell \,,$$

we make the following vector assignments for atoms and radicals:

$$K = (1,0,0,0,0), \qquad C = (0,0,0,1,0),$$
$$C\ell = (0,1,0,0,0), \qquad H = (0,0,0,0,1).$$
$$O = (0,0,1,0,0),$$

We rewrite the chemical reaction as a vector equation and seek positive integers u,v,w,x,y with no common integer factor greater than 1 so that

(16) $$u(1,1,3,0,0) + v(0,0,11,12,22) = w(0,0,2,1,0) + x(0,0,1,0,2) + y(1,1,0,0,0).$$

Setting $u = 1$ we would like to use the program of Section 4.2, but we do not have the necessary number, 6, of reactants and products. However, if we examine the actual linear system of equations,

(17) $$\begin{aligned} 1 &= 0v + 0w + 0x + y, \\ 1 &= 0v + 0w + 0x + y, \\ 3 &= -11v + 2w + x + 0y, \\ 0 &= -12v + w + 0x + 0y, \\ 0 &= -22v + 0w + 2x + 0y. \end{aligned}$$

before going to the computer program, we see that the system is dependent. The first two equations are identical.

Here we can readily recognize an independent system, however. It consists of the four different equations in (17), and we shall apply our computer program to this 4 × 4 system. (If this were not the case, we could apply the program of Section 4.2 to different combinations of 4 equations selected from the 5 until we have found an independent set of 4 equations which would yield a unique solution for the given system of all 5 equations.)

```
RUNNH
N =? 4
? 0,-11,-12,-22
? 0,2,1,0
? 0,1,0,2
? 1,0,0,0
? 1,3,0,0
 .125
 1.5
 1.375
 1

Ready
```

From the printout we see that for $u = 1$, we have

$$v = 0.125, \quad w = 1.5, \quad x = 1.375, \quad y = 1.$$

Since $0.125 = 1/8$, we can multiply all the values by 8 to balance the reaction as

(18) $$8\ KC\ell O_3 + C_{12}H_{22}O_{11} \rightarrow 12\ CO_2 + 11\ H_2O + 8\ KC\ell \,.$$

4.4 The Non-Unique Case

For our final application we shall examine a chemical reaction where the total number m of products and reactants exceeds $n + 1$, where n is the number of distinct atoms and radicals involved. The reaction reads as follows:

(19) $$CH_2O + Ag(NH_3)_2NO_3 + NaOH \rightarrow NaHCO_2 + Ag + NH_3 + NaNO_3 + H_2O \,.$$

With the following vector assignments,

$$C = (1,0,0,0,0,0), \quad Ag = (0,0,0,1,0,0),$$

$$H = (0,1,0,0,0,0), \quad N = (0,0,0,0,1,0),$$

$$O = (0,0,1,0,0,0), \quad Na = (0,0,0,0,0,1),$$

we seek positive integers s, t, u, v, w, x, y, z, with no common prime factor, so that

$$(20) \quad s(1,2,1,0,0,0) + t(0,6,3,1,3,0) + u(0,1,1,0,0,1) = v(1,1,2,0,0,1) + w(0,0,0,1,0,0) + x(0,3,0,0,1,0) + y(0,0,3,0,1,1) + z(0,2,1,0,0,0).$$

However, unlike our previous examples Equation (20) leads to a system of 6 linear equations in 8 unknowns, which we write in matrix form as

$$(21) \quad \begin{bmatrix} 1 \\ 2 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} s + \begin{bmatrix} 0 \\ 6 \\ 3 \\ 1 \\ 3 \\ 0 \end{bmatrix} t = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 3 & 0 & 2 \\ -1 & 2 & 0 & 0 & 3 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 \\ -1 & 1 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} u \\ v \\ w \\ x \\ y \\ z \end{bmatrix}$$

The system (21) has an infinite number of solutions, determined by the two parameters s and t. If we rewrite (21) as

$$\begin{bmatrix} u \\ v \\ w \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 3 & 0 & 2 \\ -1 & 2 & 0 & 0 & 3 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 \\ -1 & 1 & 0 & 0 & 1 & 0 \end{bmatrix}^{-1} \left(\begin{bmatrix} 1 \\ 2 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} s + \begin{bmatrix} 0 \\ 6 \\ 3 \\ 1 \\ 3 \\ 0 \end{bmatrix} t \right)$$

we can still use the program of Section 4.2 to assist us, but we need to use it twice. We use it once to compute the product of the inverse matrix with the column vector that precedes s, and again to compute the product of the inverse matrix with the column vector that precedes t.


```
RUNNH
N =? 6
? 0,-1,-1,0,0,-1
? 1,1,2,0,0,1
? 0,0,0,1,0,0
? 0,3,0,0,1,0
? 0,0,3,0,1,1
? 0,2,1,0,0,0
? 1,2,1,0,0,0
 .75
 1
 0
 .25
-.25
 .5

Ready
```

```
RUNNH
N =? 6
? 0,-1,-1,0,0,-1
? 1,1,2,0,0,1
? 0,0,0,1,0,0
? 0,3,0,0,1,0
? 0,0,3,0,1,1
? 0,2,1,0,0,0
? 0,6,3,1,3,0
 1.125
 0
 1
 1.875
 1.125
 .75

Ready
```

With these results we see that

$$u = 0.75s + 1.125t, \qquad x = 0.25s + 1.875t,$$
$$v = s, \qquad y = -0.25s + 1.125t,$$
$$w = t, \qquad z = 0.5s + 0.75t,$$

so that with s a positive integer multiple of 4 and t a positive integer multiple of 8 we can get an integer solution balancing the reaction. It is now possible, however, for two solutions to exist that are not mulitples of each other, in contrast to what we found in our previous problems.

With s = 4 and t = 8 we can balance the reaction as

$$(23) \quad CH_2O + 2Ag(NH_3)_2NO_3 + 3NaOH \rightarrow NaHCO_2 + 2Ag + 4NH_3 + 2NaNO_3 + 2H_2O.$$

However, if we choose s = t = 8, the balanced reaction reads as

$$(24) \quad 8CH_2O + 8Ag(NH_3)_2NO_3 + 15NaOH \rightarrow 8NaHCO_2 + 8Ag + 17NH_3 + 7NaNO_3 + 10H_2O,$$

which is not a multiple of the solution in (23). This comes about because there are 2 independent chemical reactions taking place here.

5. SUMMARY

Although this module was developed to provide some applications of matrix mathematics, these techniques are not to be considered as replacements for such chemical methods as oxidation-reduction, or the balancing of half-reactions where one learns a great deal about why and how reactions do or do not take place, in addition to how to balance them. For the chemical methods also enable one to learn a substantial amount about the properites of chemical elements. It is possible to write down a chemical reaction that does not take place and still balance it by the matrix techniques presented here! In addition, it must be pointed out again that all reactions considered in this module are electrically balanced.

Considering the example of Section 4.2, one can also see that the techniques are theoretically sound but with computer assistance one can get into some difficulty with round-off errors when larger matrices are inverted by the computer. Balancing chemical reactions without computer assistance but with the aid of generalized inverses of matrices is discussed by E.V. Krishnamurthy in [3].

6. EXERCISES

Balance the following chemical reactions:

1) $C + HNO_3 \rightarrow NO_2 + H_2O + CO_2$

2) $FeC\ell_2 + K_2Cr_2O_7 + HC\ell \rightarrow FeC\ell_3 + CrC\ell_3 + H_2O + KC\ell$

3) $HNO_3 + KMnO_4 + K_2NaCo(NO_2)_6 \rightarrow Co(NO_3)_2 + KNO_3 + NaNO_3 + Mn(NO_3)_2 + H_2O$

4) $[Co(NH_3)_5\ C\ell]C\ell_2 + KSCN \rightarrow KC\ell + [Co(NH_3)_5\ SCN]C\ell_2$

5) $H_2O_2 + NaMnO_4 + HC\ell \rightarrow MnC\ell_2 + H_2O + O_2 + NaC\ell$

7. REFERENCES

[1]. Anton, Howard. Elementary Linear Algebra, second edition. John Wiley & Sons, Inc., New York, 1977.

[2]. Fletcher, T.J. Linear Algebra Through Its Applications. Van Nostrand Reinhold Company, London, 1972.

[3]. Krishnamurthy, E.V. Generalized Matrix Inverse Approach for Automatic Balancing of Chemical Equations. International Journal of Mathematical Education in Science and Technology, 1978, Vol. 9, No. 3, pp. 323-328.

[4]. Presley, Bruce, et al. A Guide to Programming in BASIC-PLUS. The Lawrenceville School, Lawrenceville, New Jersey, 1976.

8. ANSWERS TO EXERCISES

1) $C + 4\,HNO_3 \rightarrow 4NO_2 + 2H_2O + CO_2$

2) $6FeC\ell_2 + K_2Cr_2O_7 + 14HC\ell \rightarrow 6FeC\ell_3 + 2CrC\ell_3 + 7H_2O + 2KC\ell$

3) $28HNO_3 + 11KMnO_4 + 5K_2NaCo(NO_2)_6 \rightarrow$

$5Co(NO_3)_2 + 21KNO_3 + 5NaNO_3 + 11Mn(NO_3)_2 + 14H_2O$

4) $[Co(NH_3)_5C\ell]C\ell_2 + KSCN \rightarrow KC\ell + [Co(NH_3)_5SCN]C\ell_2$

5) $(s)H_2O_2 + (t)NaMnO_4 + (u)HC\ell \rightarrow$

$(v)MnC\ell_2 + (w)H_2O + (x)O_2 + (y)NaC\ell,$

where $(u,v,w,x,y) = s(0,0,1,0.5,0) + t(3,1,1.5,1.25,1)$. For $s = 2$, $t = 4$, the reaction is balanced as

$H_2O_2 + 2NaMnO_4 + 6HC\ell \rightarrow 2MnC\ell_2 + 4H_2O + 3O_2 + 2NaC\ell.$

With $s = 10$ and $t = 4$ the reaction can be balanced as

$5H_2O_2 + 2NaMnO_4 + 6HC\ell \rightarrow 2MnC\ell_2 + 8H_2O + 5O_2 + 2NaC\ell.$

STUDENT FORM 1

Request for Help

Return to:
EDC/UMAP
55 Chapel St.
Newton, MA 02160

Student: If you have trouble with a specific part of this unit, please fill out this form and take it to your instructor for assistance. The information you give will help the author to revise the unit.

Your Name ______________________ Unit No. ______

Page ______ ○ Upper ○ Middle ○ Lower	OR	Section ______ Paragraph ______	OR	Model Exam Problem No. ______ Text Problem No. ______

Description of Difficulty: (Please be specific)

Instructor: Please indicate your resolution of the difficulty in this box.

○ Corrected errors in materials. List corrections here:

○ Gave student better explanation, example, or procedure than in unit. Give brief outline of your addition here:

○ Assisted student in acquiring general learning and problem-solving skills (not using examples from this unit.)

Instructor's Signature ______________________

Please use reverse if necessary.

Return to:
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STUDENT FORM 2

Unit Questionnaire

Name____________________ Unit No.__________ Date__________

Institution____________________ Course No.________________

Check the choice for each question that comes closest to your personal opinion.

1. How useful was the amount of detail in the unit?

____Not enough detail to understand the unit
____Unit would have been clearer with more detail
____Appropriate amount of detail
____Unit was occasionally too detailed, but this was not distracting
____Too much detail; I was often distracted

2. How helpful were the problem answers?

____Sample solutions were too brief; I could not do the intermediate steps
____Sufficient information was given to solve the problems
____Sample solutions were too detailed; I didn't need them

3. Except for fulfilling the prerequisites, how much did you use other sources (for example, instructor, friends, or other books) in order to understand the unit?

____A Lot ____Somewhat ____A Little ____Not at all

4. How long was this unit in comparison to the amount of time you generally spend on a lesson (lecture and homework assignment) in a typical math or science course?

____Much Longer ____Somewhat Longer ____About the Same ____Somewhat Shorter ____Much Shorter

5. Were any of the following parts of the unit confusing or distracting? (Check as many as apply.)

____Prerequisites
____Statement of skills and concepts (objectives)
____Paragraph headings
____Examples
____Special Assistance Supplement (if present)
____Other, please explain____________________

6. Were any of the following parts of the unit particularly helpful? (Check as many as apply.)

____Prerequisites
____Statement of skills and concepts (objectives)
____Examples
____Problems
____Paragraph headings
____Table of Contents
____Special Assistance Supplement (if present)
____Other, please explain____________________

Please describe anything in the unit that you did not particularly like.

Please describe anything that you found particularly helpful. (Please use the back of this sheet if you need more space.)