Chapter 4. Reaction balancing

4.1 Introduction

The numeric coefficients assigned to a balance equation express the relative amounts of atoms or molecules which take part to the specific reactions. More precisely tells us the proportions of moles involved therein. This fact derives directly from *Proust law* (J. L. Proust, 1750-1826) or *law of definite proportions*. It states that a given chemical compound always contains its component elements in a fixed ratio, irrespectively of the preparation route.
The quantitative aspect, dealing with mass and volume relations among reactants and products, is termed *stoichiometry*

The mole (symbol: mol) is the base unit of amount of substance in the International System of Units (SI). It is defined as exactly $6.02214076 \times 10^{23}$ elementary entities ("particles"), which may be atoms, molecules, ions, or electrons. This definition was adopted in November 2018, revising the previous definition that specified one mole as the amount of substance in 12 grams of carbon-12 (^{12}C), an isotope of carbon. Thus, for example, one mole of water (H_2O) contains $6.02214076 \times 10^{23}$ molecules, whose total mass is about 18.015 grams and the mean mass of one molecule of water is about 18.015 amu (atomic mass unit, or dalton), roughly a combined atomic mass number of 18.

Therefore, coefficients in a balanced chemical reaction can be interpreted as the relative number of moles, molecules or volume (if reactants are gases) involved in the reaction. If the chemical equation is properly balanced, the coefficients are expressed by minimal integer numbers, and they determine the quantitative aspects of the same chemical reaction. We seek a procedure that correctly establishes the coefficients of the equation; that is, the arithmetical multipliers of the different chemical units therein expressed by minimal integers, thereby providing the ultimate stoichiometric relationship.

4.2 The nullspace method

The lack of a general method in the reaction balance process causes a widespread use of iterative numerical procedures, their goal being to reach the final set of coefficients by balancing in each step a selected element or functional group.

A general method can be found with the aid of linear algebra , and many reactions, notably *redox reactions*, readily lend themselves to a convenient algebraic algorithm based on the *nullspace (or kernel) concept*. The algorithm bypasses both the oxidation number procedure or other iterative methods in a straighforward manner, and applies to complex reactions as well.

The principle of mass balance is based on the law of conservation of mass, i.e., the number of atoms of an element remains constant in a chemical reaction (we exclude nuclear reactions, where new elements may be originated). Balancing each element in a reaction imposes a set of simple equations in which the unknowns are the stoichiometric coefficients of each substance in reactants and products, provided that the chemical formula of each compound possess well established integer atomic indices, like H_2SO_4.

The whole procedure is better explained by the aid of the classical redox reaction of iron(II) sulfate with potassium permanganate in acidic water solution:

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

The law of mass conservation requires that the amount of the elements taking part to the reaction must equal in reactants (left side) and products (right side). This requires a set of 7 multiplicative stoichiometric coefficients (*a,b,c,d,e,f,g*) , like :

a FeSO4 + *b* KMnO4 + *c* H2SO4 ⟶ *d* MnSO4 + *e* Fe2(SO4)3 + *f* K2SO4 + *g* H2O

These coefficients are tied by 7 linear equations, each of them imposing the mass conservation of a single element. For example, the iron mass conservation requires that $a = 2e$, or $a - 2e = 0$ and so on for sulfur (S), oxygen (O), potassium (K),manganese (Mn) and hydrogen (H).

In the following octave script the 7 linear equation are collected in matrix **A** , which isn't a square matrix (six rows and 7 columns) being 6 the elements to balance and 7 the coefficients. The octave function *null* (**A**) is therefore able to find a vector in the nullspace of the same matrix **A .** Once the vector **Z** is found it might not be expressed by the lowest integers, so other five lines are in charge of finding the lowest integer stoichiometric coefficients.

```
% Oxidation of iron(II)sulphate with potassium permanganate.
% Coefficients finding.
clear;clc;
disp ('a FeSO4 + b KMnO4 + c H2SO4 ==> d MnSO4 + e Fe2(SO4)3 + f K2SO4 + g H2O');
A = [1  0  0  0  -2  0  0;  % Fe balance
     1  0  1  -1 -3 -1  0;  % S balance
     4  4  4 -4 -12 -4 -1;  % O balance
     0  1  0  0  0  -2  0;  % K balance
     0  1  0  -1  0  0  0;  % Mn balance
     0  0  2  0  0   0 -2]; % H balance

Z = null(A);    % Find a vector in the null space of matrix A; System Ax = b is
undetermined
x1 = min(Z);Z1 = Z./x1;
for i = 1:10    % Find the lowest stoichiometric coefficient from 1 to 10
    intZ = round(i*Z1);
    if (sum(abs(i*Z1 - intZ)))<1e-6 ;break;endif  % lowest coefficient ok
endfor

T1 = [num2str(intZ(1)),' FeSO4  + ',num2str(intZ(2)),' KMnO4  +
',num2str(intZ(3)),' H2SO4  ==> ',num2str(intZ(4)),' MnSO4  + '];
T1 = [T1,num2str(intZ(5)),' Fe2(SO4)3  + ',num2str(intZ(6)),' K2SO4  +
',num2str(intZ(7)),' H2O'];
disp('when balanced looks like : ');
disp(T1);
```

The program output pops up in the command window as follows:

```
a FeSO4 + b KMnO4 + c H2SO4 ==> d MnSO4 + e Fe2(SO4)3 + f K2SO4 + g H2O
when balanced looks like :
10 FeSO4  + 2 KMnO4  + 8 H2SO4  ==> 2 MnSO4  + 5 Fe2(SO4)3  + 1 K2SO4  + 8 H2O
```

4.3 Mass conservation between reactants and products

The correctness of the 7 coefficient might be simply tested by the elements equality, indeed 10 iron atoms are counted on the left side as well on the right, as well as 2 Mn, 2 K, 16 H, 18

S, and 80 O. The mass conservation requires some more effort, being necessary to compute the molecular masses of all the compounds. The following table is self-explaining.

Formula	Mass of one mole (g)	Stech. Coeff.	Mass in reactant (g)	Mass in product (g)
$FeSO_4$	151.91	10	1519.10	-
$KMnO_4$	158.03	2	316.06	-
H_2SO_4	98.08	8	784.64	-
$MnSO_4$	151.00	2	-	302.00
$Fe_2(SO_4)_2$	399.88	5	-	1999.4
K_2SO_4	174.26	1	-	174.26
H_2O	18.02	8	-	144.16
Total amount (g)			2619.8	2619.82

The slight difference of 0.02 g between the total mass of reagent and that of product originates from round off errors in molecular masses.

4.4 Other two reaction examples, with scripts and results

Oxidation of silver sulfide by nitric acid in HCl aqueous solution

```
clear;clc;
% Find the coefficient of a redox chemical reaction.
disp ('a Ag2S + b HNO3 + c HCl ==> d S + e AgCl + f NO(gas) + g H2O');
% oxidation of silver sulphide with nitric acid.
A = [2  0  0  0  -1  0  0;  % Ag balance
     1  0  0  -1  0  0  0;  % S balance
     0  3  0  0   0  -1 -1; % O balance
     0  1  0  0  0  -1  0;  % N balance
     0  0  1  0  -1  0  0;  % Cl balance
     0  1  1  0  0   0 -2]; % H balance

Z = null(A);     % Find a vector in the null space of matrix A; System Ax = b is undetermined
x1 = min(Z);Z1 = Z./x1;
for i = 1:10    % Find the lowest stoichiometric coefficient from 1 to 10
    intZ = round(i*Z1);
    if (sum(abs(i*Z1 - intZ)))<1e-6 ;break;endif  % lowest coefficient ok
endfor

T1 = [num2str(intZ(1)),' Ag2S  + ',num2str(intZ(2)),' HNO3  + ',num2str(intZ(3)),' HCl  ==> ',num2str(intZ(4)),' S  + '];
T1  =  [T1,num2str(intZ(5)),'  AgCl    +   ',num2str(intZ(6)),'  NO(gas)    + ',num2str(intZ(7)),' H2O'];
disp('when balanced looks like : ');
disp(T1);
```

After execution, the command window is the following :

```
a Ag2S + b HNO3 + c HCl ==> d S + e AgCl + f NO(gas) + g H2O
when balanced looks like :
3 Ag2S  + 2 HNO3  + 6 HCl  ==> 3 S  + 6 AgCl  + 2 NO(gas)  + 4 H2O
```

Oxidation of hydrogen peroxide in acid aqueous solution

```
clear;clc;
% Find the coefficient of a redox chemical reaction.
disp ('a H2O2 + b KMnO4 + c H2SO4 ==> d H2O + e O2(gas) + f MnSO4 + g K2SO4');
% oxidation of hydrogen peroxide with potassium permanganate.
A = [0  1  0  0  0  0 -2;  % K balance
     0  1  0  0  0 -1  0;  % Mn balance
     2  4  4 -1 -2 -4 -4;  % O balance (total)
     0  0  1  0  0 -1 -1;  % S balance
     2  0  2 -2  0  0  0;  % H balance
     2  0  0  0 -2  0  0]; % O balance (redox partecipating)

Z = null(A);     % Find a vector in the null space of matrix A; System Ax = b is
undetermined
x1 = min(Z);Z1 = Z./x1;
for i = 1:10    % Find the lowest stoichiometric coefficient from 1 to 10
    intZ = round(i*Z1);
    if (sum(abs(i*Z1 - intZ)))<1e-6 ;break;endif  % lowest coefficient ok
endfor

T1    =    [num2str(intZ(1)),'    H2O2       +    ',num2str(intZ(2)),'    KMnO4       +
',num2str(intZ(3)),' H2SO4  ==> ',num2str(intZ(4)),' H2O  + '];
T1   =   [T1,num2str(intZ(5)),'   O2(gas)      +   ',num2str(intZ(6)),'   MnSO4      +
',num2str(intZ(7)),' K2SO4'];
disp('when balanced looks like : ');
disp(T1);
```

After execution, the command window is the following :

```
a H2O2 + b KMnO4 + c H2SO4 ==> d H2O + e O2(gas) + f MnSO4 + g K2SO4
when balanced looks like :
5 H2O2  + 2 KMnO4  + 3 H2SO4  ==> 8 H2O  + 5 O2(gas)  + 2 MnSO4  + 1 K2SO4
```

Othe examples can be found in ref. Mazza 2022