A Mathematical Theory and Algorithms for Calibrating and Balancing Complex Chemical Reaction Functions

YINGXU WANG[1], AUDREY MA[2], and SIYUAN WANG[3]

[1] International Institute of Cognitive Informatics and Cognitive Computing (ICIC)
Laboratory for Computational Intelligence, Cognitive Systems, Software Science, and Denotational Mathematics
Dept. of Electrical and Computer Engineering
Schulich School of Engineering and Hotchkiss Brain Institute, University of Calgary
2500 University Drive NW, Calgary, Alberta, CANADA T2N 1N4
Email: yingxu@ucalgary.ca

[2] Webber Academy
1515 – 93rd Street SW
Calgary, Alberta, CANADA T3H 4A8
Email: audreyma25@gmail.com

[3] Division of Medicine
University College London
Gower Street, London, UK WC1E 6BT
Email: siyuan_wang_@hotmail.com

Abstract: It is recognized that chemical reaction balancing problems are a mathematical problem in general. A set of mathematical models is created for formalizing the problems of chemical function calibrations. The complexity of the algorithm is $O(n^2)$ that indicates the nature of the problem where n is the number of types of atoms taking part in reactions. The problem is often manually insolvable because the complexity and interlocked relations among the coefficients of elements in reaction functions. Although empirical trial-and-error and heuristic methods were proposed, they would fail when n is considerably large, i.e., n > 6. Therefore, a general mathematical model and a rigorous methodology for solving chemical reaction balancing problems are yet to be formally studied. This paper presents a theory of chemical function calibration, which enables automatic balancing of complex reaction functions by numerical algorithms based on extended systems of linear equations.

Key-Words: Mathematical theory, mathematical models, algorithm, chemical reaction functions, balancing, calibration, denotational mathematics, numerical methods, applications

1 Introduction

A chemical function is a symbolic equation of stoichiometric reactions. Both its left-hand side (LHS) and right-hand side (RHS) are a weighted sum which represent the *reactants* and the *products*, respectively. A chemical function is balanced if the weighted sums of both LHS and RHS are equal in the equation.

It is recognized that the reaction balancing problems in chemistry in general is a mathematical problem [1, 3-12, 17]. Traditional approaches to chemical reaction balancing are an empirical, trial-and-error, or heuristic process typically conducted in the following steps [7, 9, 17]:

a) Assign oxidation numbers for those atoms which change.

b) Decide on number of electrons to be shifted per atom.
c) Decide on number of electrons to be shifted per formula unit.
d) Compensate electron gain and loss by writing appropriate coefficients for the oxidizing agent and the reducing agent.
e) Insert other coefficients consistent with the conservation of matters.

Chemical reaction balancing is often a complex and tedious process especially when many elements are involved in the reaction. The complexity of chemical reaction balancing is $O(n^2)$ where n is the number of types of atoms taking part in the reaction. Because of the complexity and interlocked relations among the coefficients of elements in the reaction functions, chemical reaction balancing problems are often manually insolvable when $n > 6$.

This paper presents a set of general mathematical models and numerical algorithms for complex chemical function calibration and balancing. The nature and theoretical foundations of chemical reaction functions are explored in Section 2, which leads to the establishment of the general mathematical model of chemical reaction balancing. Numerical algorithms for formal stoichiometric balancing are developed in MATLAB in Section 3. A set of experiments and case studies is presented in Section 4 for demonstrating applications of the formal reaction balancing methodology and algorithms.

2 The Mathematical Theory of Chemical Reaction Functions

A chemical reaction function (CRF) is a symbolic equation of weighted sums of both reactants and products for denoting a stoichiometric reaction. According to the law of *conservation of matter* (atoms and ions), a chemical reaction function is balanced when the numbers of atoms of each type taking part in the reaction are the same on both sides of the function. The weighted sums of reactants and products of a CRF form a linear function. Then, solutions for the unknown weights in the CRF become a mathematical problem for calibrating the unknown coefficients of each reactant and product in a system of linear equations under certain constraints.

Definition 1. A system of *linear equations* (SLEs) is a set of m simultaneous linear functions, L_i, $1 \le i \le m$, i.e.:

$$\begin{aligned} SLE &\triangleq \mathop{R}_{i=1}^{m} L_i \\ &= \mathop{R}_{i=1}^{m} [(a_{i1}x_1 + a_{i2}x_2 + ... + a_{in}x_n) = b_i],\ m \ge n \\ &= \begin{cases} a_{11}x_1 + a_{12}x_2 + ... + a_{1n}x_n = b_1 \\ a_{21}x_1 + a_{22}x_2 + ... + a_{2n}x_n = b_2 \\ ... \\ a_{m1}x_1 + a_{m2}x_2 + ... + a_{mn}x_n = b_m \end{cases} \end{aligned} \quad (1)$$

where n is the number of variables, and the *big-R* notation represents recurring entities or repetitive functions indexed by the subscript [11, 12]. Eq. 1 can be neatly represented in the matrix form as follows:

$$\begin{aligned} SLE &\triangleq \mathbf{Ax} = \mathbf{b} \\ &= \begin{bmatrix} a_{11} & a_{12} & ... & a_{1n} \\ a_{21} & a_{22} & ... & a_{2n} \\ ... & ... & ... & ... \\ a_{m1} & a_{m2} & ... & a_{mn} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ ... \\ x_n \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ ... \\ b_m \end{bmatrix} \end{aligned} \quad (2)$$

Definition 2. Let R be a set of n_r *reactants* and P a set of n_p *products* in a chemical reaction**.** The *general form of a chemical reaction function* (CRF) can be formally represented by a linear equation, i.e.:

$$\begin{aligned} CRF &\triangleq a_1R_1 + a_2R_2 + ... + a_{n_r}R_{n_r} = \\ &\quad b_0(b_1P_1 + b_2P_2 + ... + b_{n_p}P_{n_p}) \\ &= \sum_{i=1}^{n_r} a_iR_i = b_0 \sum_{j=1}^{n_p} b_jP_j \end{aligned} \quad (3)$$

where a_i and b_j are the stoichiometric coefficients of the reactants and products, respectively, and b_0 is the least common integer multiplier of the products that makes all coefficients of the CRF as integers.

Example 1. According to Definition 2, a known reaction function, CRF_1, can be expressed as $CRF_1 \triangleq (a_1R_1 + a_2R_2 = b_0P_1) = (2\mathrm{Al} + 3\mathrm{F}_2 = 2\mathrm{AlF}_3)$ where $a_1 = 2$, $a_2 = 3$, and $b_0 = 2$ for $P_1 = \mathrm{AlF}_3$.

On the basis of Definitions 1 and 2, any CRF can be formally transformed into a general mathematical problem expressed by SLEs.

Definition 3. The *mathematical model of an arbitrary* CRF is an SLE for calibrating the set of n *reactants* **R** base on a given set of $n \times n$ *coefficients* **X** and n *product atoms* **P** in the given chemical reaction, i.e.:

$$\begin{aligned} SLE(CRF) &\triangleq \mathbf{XR} = x_0\mathbf{P},\ m = n \\ &= \mathop{R}_{k=1}^{n} [(x_{k1}R_1 + x_{k2}R_2 + \ldots + x_{kn}R_n) = x_0P_k] \\ &= \begin{cases} x_{11}R_1 + x_{12}R_2 + \ldots + x_{1n}R_n = x_0P_1 \\ x_{21}R_1 + x_{22}R_2 + \ldots + x_{2n}R_n = x_0P_2 \\ \ldots \\ x_{n1}R_1 + x_{n2}R_2 + \ldots + x_{nn}R_n = x_0P_n \end{cases} \\ &= \begin{bmatrix} x_{11} & x_{12} & \ldots & x_{1n} \\ x_{21} & x_{22} & \ldots & x_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ x_{n1} & x_{n2} & \ldots & x_{nn} \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \\ \ldots \\ R_n \end{bmatrix} = x_0 \begin{bmatrix} P_1 \\ P_2 \\ \ldots \\ P_n \end{bmatrix} \end{aligned} \tag{4}$$

where x_0 is a common integer multiplier for all products on the RHS of the reaction function.

Definition 4. The *least product multiplier*, x_0, is a commonly shared integer factor among all products that optimizes a stoichiometric function to its minimum balance where each unknown reactant coefficient, x_k, $1 \le k \le n$, obtains the minimum integer value $\mathbb{I}$, i.e.:

$$x_0 = \min_{\text{int}}(\mathop{R}_{k=1}^{n} (x_0R_k \in \mathbb{I})) \tag{5}$$

In the generic model of CRF as an SLE, the coefficient matrix **X**, as well as the reactant vector **R** and the product atom vector **P**, can be formally described in the following.

Definition 5. The *reaction coefficient matrix* **X** is an n x n square matrix where each weight coefficient is determined by the LHS of the given CRF with respect to each atom in the reactant vector **R**, R^a, i.e.:

$$\mathbf{X} = \mathop{R}_{i=1}^{n}\mathop{R}_{j=1}^{n} x_{ij} = \begin{bmatrix} x_1 & x_2 & \ldots & x_n & R_i^a \\ x_{11} & x_{12} & \ldots & x_{1n} & R_1^a \\ x_{21} & x_{22} & \ldots & x_{2n} & R_2^a \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ x_{n1} & x_{n2} & \ldots & x_{nn} & R_n^a \end{bmatrix} \tag{6}$$

Example 2. Reconsider the problem in Example 1, $CRF_1 \triangleq 2\text{Al} + 3\text{F}_2 = 2\text{AlF}_3$, as an SLE as follows where $x_0 = 2$:

$$\mathbf{X} = \begin{bmatrix} x_1 & x_2 & R_i^a \\ 1 & 0 & Al \\ 0 & 2 & F \end{bmatrix} \mathbf{R} = \begin{bmatrix} x_1(\text{Al}) \\ x_1(F) \end{bmatrix} \mathbf{P} = \begin{bmatrix} P_1(Al) \\ P_2(F) \end{bmatrix} = \begin{bmatrix} 1 \\ 3 \end{bmatrix} \tag{7}$$

Example 3. Given the following chemical reaction:

$$\begin{aligned} &4\text{Cr}(\text{N}_2\text{H}_4\text{CO})_6 + 3\text{Cr}(\text{CN})_6 + x_1\text{KMnO}_4 + x_2\text{H}_2\text{SO}_4 \\ &\rightarrow x_3\text{K}_2\text{Cr}_2\text{O}_7 + x_4\text{MnSO}_4 + x_5\text{CO}_2 + x_6\text{KNO}_3 \\ &\quad + x_7\text{K}_2\text{SO}_4 + x_8\text{HO}_2 \end{aligned} \tag{8}$$

Because there are eight atoms taking part in the reaction, eight independent equations are required in the SLE for solving the eight unknown coefficients. In order to do so, all known product values are moved on the RHS of the function, while only eight unknown elements remain on the LHS. This result in the following normalized CRF:

$$\begin{aligned} &-x_1\text{KMnO}_4 - x_2\text{H}_2\text{SO}_4 + x_3\text{K}_2\text{Cr}_2\text{O}_7 + x_4\text{MnSO}_4 \\ &+x_5\text{CO}_2 + x_6\text{KNO}_3 + x_7\text{K}_2\text{SO}_4 + x_8\text{HO}_2 \\ &= 4\text{Cr}(\text{N}_2\text{H}_4\text{CO})_6 + 3\text{Cr}(\text{CN})_6 \end{aligned} \tag{9}$$

All parameters **X**, **R** and **P** in the SLE for the given CRF can be determined with respect to each of the atoms in the reaction, respectively, i.e.:

$$\mathbf{X} = \begin{bmatrix} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 & x_8 & R_i^a \\ -1 & 0 & 2 & 0 & 0 & 1 & 2 & 0 & K \\ -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & Mn \\ -4 & -4 & 7 & 4 & 2 & 3 & 4 & 1 & O \\ 0 & -2 & 0 & 0 & 0 & 0 & 0 & 2 & H \\ 0 & -1 & 0 & 1 & 0 & 0 & 1 & 0 & S \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & Cr \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & C \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & N \end{bmatrix}$$

$$\mathbf{R} = \begin{bmatrix} x_1(\mathrm{KMnO_4}) \\ x_2(\mathrm{H_2SO_4}) \\ x_3(\mathrm{K_2Cr_2O_7}) \\ x_4(\mathrm{MnSO_4}) \\ x_5(\mathrm{CO_2}) \\ x_6(\mathrm{KNO_3}) \\ x_7(\mathrm{K_2SO_4}) \\ x_8(\mathrm{HO_2}) \end{bmatrix} \quad \mathbf{P} = \begin{bmatrix} P_1(K) \\ P_2(Mn) \\ P_3(O) \\ P_4(H) \\ P_5(S) \\ P_6(Cr) \\ P_7(C) \\ P_8(N) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 24 \\ 96 \\ 0 \\ 7 \\ 42 \\ 66 \end{bmatrix} \tag{10}$$

Lemma 1. The *existence of a unique solution* for an SLE is that the number of independent equations m must be greater or equal to the number of variables n, i.e.:

$$m \geq n \tag{11}$$

Lemma 2. The *criterion for optimal reaction balancing* is to obtain a set of the least reactant and product coefficients determined by x_0.

Without the minimum criterion as stated in Lemma 1, there would be multiple solutions for balancing an arbitrary CRF.

Theorem 1. Given any CRF expressed as a system of linear equations, $SLE(CRF) \triangleq \mathbf{XR} = \mathbf{P}$, there exists a unique solution when at least n independent linear equations are obtained for each of the n types of atoms involved in the reaction, i.e.:

$$\mathbf{R} = \mathop{R}_{x_0=1}^{n_{\max}}(\mathbf{X} \setminus (x_0\mathbf{P})), x_0 = \min_{\text{int}}(\mathop{R}_{k=1}^{n}(x_0 R_k \in \mathbb{I})) \tag{12}$$

where the iterative limit $n_{\max} \leq 100$, typically.

Proof. On the basis of Definition 3, the solution of any CRF can be expressed in the form of Eq. 4. Because there are $n = m$ linear equations for the set of unknown reactant atoms $|\mathbf{R}|$ in the CRF, according to the condition of Lemma 1, Eq. 4 can be uniquely solved.

■

It is noteworthy that the SLE solution presented in Theorem 1 is a calibration of values of the reactant vector **R** by given **X** and **P**.

Example 4. The chemical reaction as given in Examples 1 and 2, $CRF_1 = x_1\mathrm{Al} + x_2\mathrm{F_2} \rightarrow x_0\mathrm{AlF_3}$, can be formally described as an SLE according to Definition 3 as follows:

$$\begin{aligned} SLE(CRF_1) &\triangleq \mathbf{XR} = x_0\mathbf{P} \\ &= \begin{cases} x_{11}R_1(\mathrm{Al}) + x_{12}R_2(\mathrm{F}) = x_0P_1(\mathrm{Al}) \\ x_{21}R_1(\mathrm{Al}) + x_{22}R_2(\mathrm{F}) = x_0P_2(\mathrm{F}) \end{cases} \\ &= \begin{cases} R_1(\mathrm{Al}) + 0R_2(\mathrm{F}) = x_0P_1(\mathrm{Al}) \\ 0R_1(\mathrm{Al}) + 2R_2(\mathrm{F}) = 3x_0P_2(\mathrm{F}) \end{cases} \\ &= \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} x_1(\mathrm{Al}) \\ x_1(F) \end{bmatrix} = x_0 \begin{bmatrix} 1 \\ 3 \end{bmatrix} \end{aligned} \tag{13}$$

Then, the balance of $SLE(CRF_1)$ is solved according to Theorem 1 as follows:

$$\begin{aligned} \mathbf{R} &= \begin{bmatrix} x_1(\mathrm{Al}) \\ x_2(\mathrm{F}) \end{bmatrix} = \mathbf{X} \setminus x_0\mathbf{P} \\ &= \begin{cases} \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} \setminus x_0 \begin{bmatrix} 1 \\ 3 \end{bmatrix} = \begin{bmatrix} 1 \\ 1.5 \end{bmatrix}, & x_0 = 1 \\ \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} \setminus x_0 \begin{bmatrix} 1 \\ 3 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \end{bmatrix}, & x_0 = 2 \end{cases} \\ &\Rightarrow 2\mathrm{Al} + 3\mathrm{F_2} = 2\mathrm{AlF_3} \end{aligned} \tag{14}$$

That is, the reaction can be optimally balanced as: $2\mathrm{Al} + 3\mathrm{F_2} = 2\mathrm{AlF_3}$ with minimum integer coefficients for each atom when the least common multiplier $x_0 = 2$ is determined.

Corollary 1. The *conservative rule* for chemical reactions states that the number of atoms, a_k, $1 \leq k \leq n$, remains the same between the elements of reactants ($R(a_k)$) and products ($P(a_k)$), i.e.:

$$\sum_{k=1}^{n}(x_k R(a_k) - x_0 P(a_k)) = 0 \tag{15}$$

where n is the number of types of atoms taking part in the chemical reaction.

Corollary 1 is a formal description of the law of conservation of matter in chemistry [4, 6, 7, 9],

which states that matter (atom or iron) is neither created nor destroyed in a chemical process. It is an instance of the principle of general system equilibrium [12, 15].

It is noteworthy that, although Theorem 1 and Lemma 1 guarantee the existence of a unique solution to any formally expressed SLE of arbitrary CRFs, not all of them may be manually solved. For instance, the complex reaction function as given in Example 3 cannot be easily balanced in empirical approaches without the support of a computational algorithm that implements Theorem 1 as a tool.

3 Numerical Algorithms for Balancing Complex Stoichiometric Functions

The mathematical models and examples presented in Section 2 indicate that the stoichiometric balancing problems would be extremely complicated to be solved manually. The challenging problems may be classified into two categories known as: a) Insufficient independent equations can be established constrained by the number of types of atoms in the function; and b) The need for calibrating a set of least reactant coefficients under the constraint of (a).

The strategy for solving Problem (a) is to reduce the number of unknown reactant coefficients to be the same as that of the types of atoms on the LHS of the function according to Lemma 1. This method is called reaction function normalization.

Definition 6. The *normalization of a CRF* is a preprocessing process that reduces the number of unknown reactant coefficients m to be the same as that of the types of atoms n on the LHS of a reaction function. The rest unknown reactant coefficients are moved to the RHS of the function with a sign change for their coefficients where all products share a common integer multiplier x_0.

The strategy for solving Problem (b) is to optimize the solutions with respect to the least product coefficients x_0. In both strategies, suitable numerical methods and algorithms are required because of the extreme complexity in solving the chemical reaction balancing problems.

3.1 The Direct Algorithm for Balancing CRFs

According to Theorem 1, there exists a unique numerical solution for any CRF when it is represented by a sufficient SLE no matter how complex it is. A direct matrix-based algorithm for solving an SLE of chemical reaction balancing is presented in the following algorithm implemented in MATLAB.

Algorithm 1. The *algorithm for direct chemical reaction balancing* (DCRB) is designed on the basis of the mathematical models as given in Definition 3 and Theorem 1 as shown in Fig. 1 in MATLAB.

The DCRB algorithm solves general reaction balancing problems by an SLE with the known coefficient matrix **X** and the product vector **P**. The inputs of the algorithm are the coefficient matrix of the reactant atoms (**X**) and the product vector (**P**). The outputs of the algorithm are the adjusted integer solutions for all reactants (**R**), products (**P**), and the least common multiplier among the coefficient (x_0) that optimizes all elements to the minimum integer.

Algorithm 1. The DCRB Algorithm

```
function [R, x0] = DCRB(X, P)
% Author: Y. Wang et al., 2016

% R – The reactant vector
% P – The product vector
% X – The coefficient matrix of reactant atoms
% imax – the maximum iteration
% tol – numerical tolerance of accuracy

% Step 0: Initialization
[n] = size (P);
R = zeros(n);
imax = 20;
tol = 0.0001;

% Step 1: Linear calibration
R = X \ P;

% Step 2: Balancing optimization
s = sum(R);
for k = 1 : imax
    r = abs((k*s - round(k*s)) / s);
    if (r <= tol)
        break;
    end
end;
x0 = k;
R = k * R;
```

Fig. 1. The algorithm of direct chemical reaction balancing

DCRB detects the size of the problem represented by that of the products |**P**|, which is equivalent to the number of types of reactant atoms, n, in the

reaction. The values of all reactants (**R**) ar e determined by a left division, **R** = **X** \ **P**, based on the given coefficient matrix **X** and product vector **P**. Then, the optimization of the results for finding the least product multiplier x_0 is carried out by checking the minimum suitable x_0 as the common multiplier in the balance from the bottom up until it makes each coefficient of **R** and **P** to be an integer.

It is noteworthy because there are often more unknown coefficients than the number of types of atoms n in CRF balancing, a p reprocessing step is taken for normalizing the reaction expression according to Definition 6 before executing the DCRN algorithm.

3.2 The Iterative Algorithm for Balancing CRFs

An iterative algorithm for solving the SLE of CRF balancing problems can be designed based on t he Gauss-Seidel method [2, 16].

Algorithm 2. The ICRB Algorithm

```
function [R] = ICRB(X, P)
% Author: Y. Wang et al., 2016

% Step 0: Initialization
n = size(P);
R = zeros(n);
x = R;
s = R;
satisfaction = 0;
imax = 100;
tol = 0.0001;

% Step 1: Iterative calibration
for k = 1 : imax
    for i = 1 : n
        s(i) = 0;
        R = x;
        for j = 1 : n
            if i ~= j
               s(i) = s(i) + (X(i, j) * x(j));
            end
        end
        x(i) = (P(i) - s(i)) / X(i, i);
        if abs((R(i) - x(i)) / R(i)) <= tol
           satisfaction = 1;
        end
    end
    if satisfaction == 1
       break
    end
end
R = x;

% Step 2: Balancing optimization
s = sum(R);
for k = 1 : imax
    r = abs((k*s - round(k*s)) / s);
    if (r <= tol)
        break;
    end
end;
x0 = k;
R = k * R:
```

Fig. 2. The algorithm of iterative chemical reaction balancing

Definition 7. The classic Gauss-Seidel method [2] for solving SLEs is a series of iterative refinements of the solutions x_i, $1 \le i \le n$, as follows:

$$x_i = \begin{cases} x_1^{(k+1)} = \frac{1}{a_{11}}(b_1 - \sum_{j=2}^{n} a_{1j} x_j^{(k)}) \\ x_i^{(k+1)} = \frac{1}{a_{ii}}(b_i - (\sum_{j=1}^{i-1} a_{ij} x_j^{(k+1)} - \sum_{j=i+1}^{n} a_{ij} x_j^{(k)})), \ i = 2,...,n-1 \\ x_n^{(k+1)} = \frac{1}{a_{nn}}(b_n - \sum_{j=1}^{n-1} a_{nj} x_j^{(k+1)}) \end{cases} \quad (16)$$

Definition 8. An improved Gauss-Seidel method for solving SLEs is optimized and simplified in [16] as follows:

$$x_i = \frac{1}{a_{ii}}(b_i - \sum_{j=1 \wedge j \neq i}^{n} a_{ij} x_j) \quad (17)$$

where the three segments in Eq. 16 are unified in Eq. 17, and all round-end updating are replaced by on-fly updating within the same iteration in order to accelerate the speed of the algorithm.

Algorithm 2. The *algorithm for iterative chemical reaction balancing* (ICRB) is designed based on the improved Gauss-Seidel method as given in Definition 8, which is implemented in MATLAB as shown in Fig. 2.

The ICRB algorithm solves general reaction balancing problems as an SLE by iterative approximating. The inputs of the algorithm are the coefficient matrix of the reactant atoms (**X**) and the product vector (**P**). The outputs of the algorithm are adjusted integer solutions for all reactants (**R**) and products (**P**) according to the optimal balancing results. The ICRB algorithm implements the enhanced Gauss-Seidel iterative strategy as provided in Definition 8 for approximating towards an accurate solution for the given SLE(CRB) problem. It is then optimized by be x_0 in order to calibrate a set of least integer coefficients for **R** and **P**.

4 Experiments and Applications of the Formal Methodologies for Solving CRFs

On the basis of the algorithms developed in preceding section, arbitrary CRF balancing problems can be automatically solved applying the algorithms in MATLAB. This section presents a set of experimental results and case studies on complex CRF balancing problems in order to demonstrate the power and applications of the formal methodology and algorithms.

Example 5. A chemical reaction is observed as follows that involves three types of atoms C, H, and O in the reaction:

$$x_1 C_2H_6 + x_2 O_2 \rightarrow x_3 CO_2 + x_0 H_2O \quad (18)$$

Because there are four unknown coefficients but only three types of atoms for building a set of independent equations, it is insufficient to solve the problem as given. Therefore, the reaction expression must be normalized by CRF_2 below according to Definition 6 where arbitrary three elements containing each of the reactant atoms are represented on the LHS of the function such as:

$$CRF_2 \triangleq x_1 C_2H_6 + x_2 O_2 - x_3 CO_2 = x_0 H_2O \quad (19)$$

where x_0 is the given common multiplier that will be determined iteratively by the algorithm.

Then, the problem is formally represented as an SLE for automatic balancing according to Theorem 1 as follows:

$$SLE(CRF_2) \triangleq \mathbf{XR} = \mathbf{P}$$
$$= \begin{bmatrix} 2 & 0 & -1 \\ 6 & 0 & 0 \\ 0 & 2 & -2 \end{bmatrix} \begin{bmatrix} x_1(C_2H_6) \\ x_2(O_2) \\ x_3(CO_2) \end{bmatrix} = x_0 \begin{bmatrix} 0 \\ 2 \\ 1 \end{bmatrix} \quad (20)$$

Applying Algorithm 1 or 2, the problem SLE(CRF_2) is solved where $\mathbf{R} = [x_1(C_2H_6), x_2(O_2), x_3(CO_2)]^T = [2, 7, 4]^T$, and $x_0 = 6$. It yields the balanced CRF_2 as:

$$CRF_2: 2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O \quad (21)$$

Example 6. A chemical reaction is observed as follows that involves three types of atoms Zn, O, and H in the reaction:

$$x_1\mathrm{Zn}^+ + x_2\mathrm{OH}^- \rightarrow x_3\mathrm{O}_2 + x_4\mathrm{Zn}^+ + x_5\mathrm{H}_2\mathrm{O} \quad (22)$$

The reaction expression is normalized by CRF_3 as follows in order to solve it uniquely according to Theorem 1:

$$CRF_3 \triangleq x_1\mathrm{Zn}^+ + x_2\mathrm{OH}^- - x_3\mathrm{O}_2 = x_0(\mathrm{Zn}^+ + \mathrm{H}_2\mathrm{O}) \quad (23)$$

Its equivalent mathematical expression is as follows:

$$SLE(CRF_3) \triangleq \mathbf{XR} = \mathbf{P}$$
$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -2 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x_1(\mathrm{Zn}^+) \\ x_2(\mathrm{OH}^-) \\ x_3(\mathrm{H}) \end{bmatrix} = x_0 \begin{bmatrix} 1 \\ 1 \\ 2 \end{bmatrix} \quad (24)$$

The problem SLE(CRF_3) is solved by Algorithm 1 or 2 where $\mathbf{R} = [x_1(\mathrm{Zn}^+), x_2(\mathrm{OH}^-), x_3(\mathrm{O}_2)]^{\mathrm{T}} = [2, 4, 1]^{\mathrm{T}}$ and $x_0 = 2$. It yields the balanced CRF_3 as:

$$CRF_3\text{: } 2\mathrm{Zn}^+ + 4\mathrm{OH}^- = \mathrm{O}_2 + 2\mathrm{Zn}^+ + 2\mathrm{H}_2\mathrm{O} \quad (25)$$

Example 7. A chemical reaction is observed as follows that involves five types of atoms Pb, O, H, Hg, and Cl in the reaction:

$$x_1\mathrm{PbO}_2 + x_2\mathrm{H}^+ + x_3\mathrm{Hg} + x_4\mathrm{Cl}^- \rightleftharpoons x_5\mathrm{H}_2\mathrm{O} + x_6\mathrm{Pb}^{2+} + x_7\mathrm{Hg}_2\mathrm{Cl}_2 \quad (26)$$

The reaction expression is normalized by CRF_4 as follows in order to solve it uniquely according to Theorem 1:

$$CRF_4 \triangleq x_1\mathrm{PbO}_2 + x_2\mathrm{H}^+ + x_3\mathrm{Hg} + x_4\mathrm{Cl}^- - x_5\mathrm{H}_2\mathrm{O} = x_0(\mathrm{Pb}^{2+} + \mathrm{Hg}_2\mathrm{Cl}_2) \quad (27)$$

Its equivalent mathematical expression is as follows:

$$SLE(CRF_4) \triangleq \mathbf{XR} = \mathbf{P}$$
$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & -2 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x_1(\mathrm{PbO}_2) \\ x_2(\mathrm{H}^+) \\ x_3(\mathrm{Hg}) \\ x_4(\mathrm{Cl}^-) \\ x_5(\mathrm{H}_2\mathrm{O}) \end{bmatrix} = x_0 \begin{bmatrix} 1 \\ 0 \\ 0 \\ 2 \\ 2 \end{bmatrix} \quad (28)$$

The problem SLE(CRF_4) is solved by Algorithm 1 or 2 where $\mathbf{R} = [x_1(\mathrm{PbO}_2), x_2(\mathrm{H}^+), x_3(\mathrm{Hg}), x_4(\mathrm{Cl}^-), x_5(\mathrm{H}_2\mathrm{O})]^{\mathrm{T}} = [1, 4, 2, 2, 2]^{\mathrm{T}}$ and $x_0 = 1$. It yields the balanced CRF_4 as:

$$CRF_4\text{: } \mathrm{PbO}_2 + 4\mathrm{H}^+ + 2\mathrm{Hg} + 2\mathrm{Cl}^- \rightleftharpoons 2\mathrm{H}_2\mathrm{O} + \mathrm{Pb}^{2+} + \mathrm{Hg}_2\mathrm{Cl}_2 \quad (29)$$

Example 8. A chemical reaction is observed as follows that involves five types of atoms U, O, H, Ag, and Cl in the reaction:

$$x_1\mathrm{UO}_2^{2+} + x_2\mathrm{H}^+ + x_3\mathrm{Ag} + x_4\mathrm{Cl}^- \rightleftharpoons x_5\mathrm{U}^{4+} + x_6\mathrm{AgCl} + x_7\mathrm{H}_2\mathrm{O} \quad (30)$$

The reaction expression is normalized by CRF_5 as follows in order to solve it uniquely according to Theorem 1:

$$CRF_5 \triangleq x_1\mathrm{UO}_2^{2+} + x_2\mathrm{H}^+ + x_3\mathrm{Ag} + x_4\mathrm{Cl}^- - x_5\mathrm{U}^{4+} = x_0(\mathrm{AgCl} + \mathrm{H}_2\mathrm{O}) \quad (31)$$

Its equivalent mathematical expression is as follows:

$$SLE(CRF_5) \triangleq \mathbf{XR} = \mathbf{P}$$
$$= \begin{bmatrix} 1 & 0 & 0 & 0 & -1 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x_1(\mathrm{UO}_2^{2+}) \\ x_2(\mathrm{H}^+) \\ x_3(\mathrm{Ag}) \\ x_4(\mathrm{Cl}^-) \\ x_5(\mathrm{U}^{4+}) \end{bmatrix} = x_0 \begin{bmatrix} 0 \\ 1 \\ 2 \\ 1 \\ 1 \end{bmatrix} \quad (32)$$

The problem SLE(CRF_5) is solved by Algorithm 1 or 2 where

$\mathbf{R} = [x_1(UO_2^{2+}), x_2(H^+), x_3(Ag), x_4(Cl^-), x_5(U^{4+})]^T = [1, 4, 2, 2, 1]^T$ and $x_0 = 2$. That yields the balanced CRF_5 as:

$$CRF_5: UO_2^{2+} + 4H^+ + 2Ag + 2Cl^- \rightleftharpoons U^{4+} + 2AgCl + 2H_2O \quad (33)$$

Example 9. Reconsidering the CRF as given in Example 3, it is a complex case where eight types of atoms, i.e., K, Mn, O, H, S, Cr, C, and N, take part in the reaction:

$$4Cr(N_2H_4CO)_6 + 3Cr(CN)_6 + x_1KMnO_4 + x_2H_2SO_4 \rightarrow x_3K_2Cr_2O_7 + x_4MnSO_4 + x_5CO_2 + x_6KNO_3 + x_7K_2SO_4 + x_8HO_2 \quad (34)$$

The reaction expression is normalized by CRF_6 as follows in order to uniquely solve it according to Theorem 1:

$$\begin{aligned} CRF_6 \triangleq & -x_1KMnO_4 - x_2H_2SO_4 + x_3K_2Cr_2O_7 \\ & + x_4MnSO_4 + x_5CO_2 + x_6KNO_3 \\ & + x_7K_2SO_4 + x_8HO_2 \\ & = x_0[4Cr(N_2H_4CO)_6 + 3Cr(CN)_6] \end{aligned} \quad (35)$$

Its equivalent mathematical expression is as follows:

$$SLE(CRF_6) \triangleq \mathbf{XR} = \mathbf{P}$$

$$= \begin{bmatrix} -1 & 0 & 2 & 0 & 0 & 1 & 2 & 0 \\ -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ -4 & -4 & 7 & 4 & 2 & 3 & 4 & 1 \\ 0 & -2 & 0 & 0 & 0 & 0 & 0 & 2 \\ 0 & -1 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_1(KMnO_4) \\ x_2(H_2SO_4) \\ x_3(K_2Cr_2O_7) \\ x_4(MnSO_4) \\ x_5(CO_2) \\ x_6(KNO_3) \\ x_7(K_2SO_4) \\ x_8(HO_2) \end{bmatrix} = x_0 \begin{bmatrix} 0 \\ 0 \\ 24 \\ 96 \\ 0 \\ 7 \\ 42 \\ 66 \end{bmatrix} \quad (36)$$

where **X, R,** and **P** have been derived in Eq. 10, respectively.

The problem SLE(CRF_6) is solved by Algorithm 1 or 2 where $\mathbf{R} = [x_1(KMnO_4), x_2(H_2SO_4), x_3(K_2Cr_2O_7), x_4(MnSO_4), x_5(CO_2), x_6(KNO_3), x_7(K_2SO_4), x_8(HO_2)]^T = [1176, 1399, 35, 1176, 420, 660, 223, 1879]^T$ and $x_0 = 10$. It yields the balanced CRF_6 as:

$$\begin{aligned} CRF_6: & 40Cr(N_2H_4CO)_6 + 30Cr(CN)_6 \\ & + 1176KMnO_4 + 1399H_2SO_4 \\ & = 35K_2Cr_2O_7 + 1176MnSO_4 + 420CO_2 \\ & + 660KNO_3 + 223K_2SO_4 + 1879HO_2 \end{aligned} \quad (37)$$

All experiments in Examples 5 through 9 demonstrate that no matter how complex it would be, the general methodology as presented in Theorem 1 and Algorithms 1 or 2 can efficiently solve arbitrary CRF problems as an SLE for stoichiometric reaction calibration and balancing.

5 Conclusion

It has been recognized that stoichiometric reaction balancing problems are a mathematical problem. The theoretical foundations of chemical reaction functions and their balancing have been explored. This has led to the establishment of a theory and methodology for formal stoichiometric reaction balancing. Numerical algorithms for formal reaction balancing have been implemented in MATLAB for automatically solving any complex reaction balancing problems in chemistry.

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