

Balancing Chemical Equations

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Abstract

Balancing chemical equations is a basic problem in chemistry. An easy and commonly employed method is to convert the task to a linear algebra problem. We use the row-reduced echelon form of the coefficient matrix which gives directly a basis for its null space. The dimension of the null space indicates how many basic mathematically balanced chemical equations are necessary to generate all balanced reactions. If we impose the reactants and the products, the algebraic structure of the solution set is not a subspace but a cone. The problem is now to determine all extreme rays of a cone, or all extreme points of a convex polyhedral set, it is a vertex enumeration problem, which is a hard one in algorithmic.

1 Introduction

Balancing chemical equations is a basic problem in chemistry. An easy and commonly used method to solve such problems is to convert it to the task of solving a linear homogeneous system. The set of solutions of the linear system, the null space of the coefficient matrix, leads to a set of mathematically balanced chemical equations. This null space is easily obtained from the row reduced echelon form of the coefficient matrix. In this case it is the

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mathematical solution who fix the reactants and the products. The dimension of the null space indicates how many basic mathematically balanced chemical equations are necessary to generate all possible mathematically balanced reactions. Indeed, any linear combination of the basic mathematically balanced chemical equations is a mathematically balanced chemical equation. It is important to mention that even if a chemical equation is mathematically balanced, it does not assure that it will be experimentally observed.

If we impose the reactants and the products, the solution is again in the null space but there are restrictions on the possible solutions. The algebraic structure of the set of solutions is a pointed convex polyhedral cone, and to determine the possible solutions we need to find its extreme rays. It is equivalent to find the extreme points of a convex polyhedron, and it is an occurrence of the vertex enumeration problem, which is known to be a hard problem [8]. It means that the effort (time) to solve the problem depends on the dimension of the null space involved.

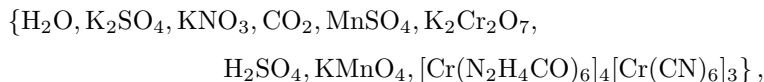
The organization of this paper is as follows. We present 3 examples to illustrate the way to find all the possible mathematically balanced chemical equations for a given problem. In Section 2, a basic simple problem is solved. We remind how the null space is directly obtained from the row reduced echelon form of the coefficient matrix. The mathematical solution fixes the reactants and the products. In the first part of Sections 3, we consider finding reactions without fixing the reactants and the products, as considered in Section 2. We focus on the row reduced echelon form of the coefficient matrix and to its null space. In the second part of Section 3, we introduce a method for the determination of a convex polyhedral cone which corresponds to the set of possible solutions when the reactants and the products are given. Finally, a problem with a higher dimensional null space is considered in Section 4.

2 A one-parameter example

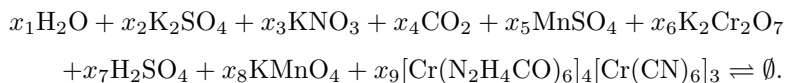
This first example is a standard basic problem of balancing chemical equation supposed to be “hard” to balance [5,10]. Several methods to solve this

problem are equivalent to solving it by inspection, see [6] and recently [9]. Other methods consider the row reduced echelon form of the coefficient matrix as we will illustrate in this section.

The molecules of the reaction are



and we look for x_i ($i = 1, \dots, 9$) such that



In the sequel the symbol $\rightleftharpoons$ means that the reaction can be read from left to right or from right to left, both directions are mathematically possible.

The coefficient matrix of the corresponding set of molecules is

$$\Sigma = \begin{bmatrix} \text{H} & : & 2 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 96 \\ \text{S} & : & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ \text{N} & : & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 66 \\ \text{C} & : & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 42 \\ \text{Mn} & : & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ \text{Cr} & : & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 7 \\ \text{K} & : & 0 & 2 & 1 & 0 & 0 & 2 & 0 & 1 & 0 \\ \text{O} & : & 1 & 4 & 3 & 2 & 4 & 7 & 4 & 4 & 24 \end{bmatrix},$$

and its row reduced echelon form is

$$\text{RREF}(\Sigma) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1879/10 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 223/10 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 66 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 42 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 588/5 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 7/2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & -1399/10 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -588/5 \end{bmatrix} = \begin{bmatrix} I_8 & N \end{bmatrix}.$$

Since

$$\begin{bmatrix} I_8 & N \end{bmatrix} \begin{bmatrix} -N \\ I_1 \end{bmatrix} = -I_8 N + N I_1 = O,$$

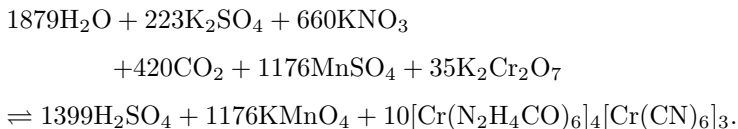
the column, or any multiple of this column,

$$\begin{bmatrix} -N \\ I_1 \end{bmatrix} = \begin{bmatrix} -1879/10 \\ -223/10 \\ -66 \\ -42 \\ -588/5 \\ -7/2 \\ 1399/10 \\ 588/5 \\ 1 \end{bmatrix}$$

form a basis for the null space of Σ . The null space is a one dimensional subspace of $\mathbb{R}^9$ and a basis with integer entries is for example

$$(1879, 223, 660, 420, 1176, 35, -1399, -1176, -10),$$

which leads to the mathematically balanced chemical equation

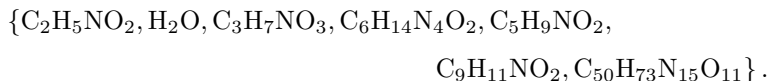


So this equation determine the set of reactants and the set of products, which depends on the direction we read the equation.

Other problems, which at first seemed complicated to solve [2, 7, 9], can be easily solved by the same method. This is always the case when the dimension of the null space of Σ is 1.

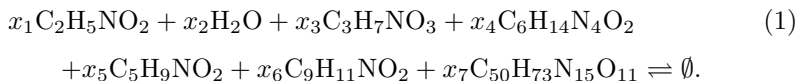
3 First multi-parameter example

We consider the following set of molecules for a reaction [2]



3.1 Free sets of reactants and products

We look for x_i ($i = 1, \dots, 7$) such that



The coefficient matrix is

$$\Sigma = \begin{bmatrix} \text{C} & : 2 & 0 & 3 & 6 & 5 & 9 & 50 \\ \text{H} & : 5 & 2 & 7 & 14 & 9 & 11 & 73 \\ \text{N} & : 1 & 0 & 1 & 4 & 1 & 1 & 15 \\ \text{O} & : 2 & 1 & 3 & 2 & 2 & 2 & 11 \end{bmatrix},$$

and its row reduced echelon form is

$$\text{RREF}(\Sigma) = \begin{bmatrix} 1 & 0 & 0 & 0 & -6 & -12 & -41 \\ 0 & 1 & 0 & 0 & -1/3 & -3 & -15 \\ 0 & 0 & 1 & 0 & 13/3 & 9 & 32 \\ 0 & 0 & 0 & 1 & 2/3 & 1 & 6 \end{bmatrix} = \begin{bmatrix} I_4 & N \end{bmatrix}.$$

Since

$$\begin{bmatrix} I_4 & N \end{bmatrix} \begin{bmatrix} -N \\ I_3 \end{bmatrix} = -I_4 N + N I_3 = O,$$

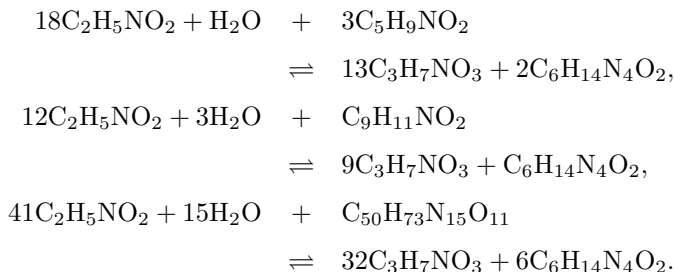
the columns of

$$\begin{bmatrix} -N \\ I_3 \end{bmatrix} = \begin{bmatrix} 6 & 12 & 41 \\ 1/3 & 3 & 15 \\ -13/3 & -9 & -32 \\ -2/3 & -1 & -6 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

form a basis for the null space of Σ . The dimension of the null-space is 3, and we can consider, with scaling, that a basis is the following set

$$\{(18, 1, -13, -2, 3, 0, 0), (12, 3, -9, -1, 0, 1, 0), (41, 15, -32, -6, 0, 0, 1)\}.$$

Each element of this basis leads to a mathematically balanced equation which can be read in both direction



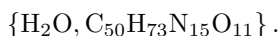
Any linear combination of these equations leads to a mathematically balanced equation.

3.2 Fixed sets of reactants and products

Now, suppose that we fix the set of reactants and the set of products to be respectively



and



We would like to balance (1) with $x_1 \geq 0$, $x_2 \leq 0$, $x_3 \geq 0$, $x_4 \geq 0$, $x_5 \geq 0$, $x_6 \geq 0$, and $x_7 \leq 0$.

We consider a linear combination of the elements of the basis of the null-space

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \end{bmatrix} = \alpha_1 \begin{bmatrix} 18 \\ 1 \\ -13 \\ -2 \\ 3 \\ 0 \\ 0 \end{bmatrix} + \alpha_2 \begin{bmatrix} 12 \\ 3 \\ -9 \\ -1 \\ 0 \\ 1 \\ 0 \end{bmatrix} + \alpha_3 \begin{bmatrix} 41 \\ 15 \\ -32 \\ -6 \\ 0 \\ 0 \\ 1 \end{bmatrix},$$

to get the following set of inequalities

$$\left\{ \begin{array}{lclclcl} x_1 & = & 18\alpha_1 & + & 12\alpha_2 & + & 41\alpha_3 & \geq & 0, \\ x_2 & = & \alpha_1 & + & 3\alpha_2 & + & 15\alpha_3 & \leq & 0, \\ x_3 & = & -13\alpha_1 & - & 9\alpha_2 & - & 32\alpha_3 & \geq & 0, \\ x_4 & = & -2\alpha_1 & - & \alpha_2 & - & 6\alpha_3 & \geq & 0, \\ x_5 & = & 3\alpha_1 & & & & & \geq & 0, \\ x_6 & = & & & \alpha_2 & & & \geq & 0, \\ x_7 & = & & & & & \alpha_3 & \leq & 0. \end{array} \right. \quad (2)$$

If $\alpha^i = (\alpha_1^i, \alpha_2^i, \alpha_3^i)$ ($i = 1, 2$) satisfy these inequalities, for any $\lambda_i \geq$

0 ($i = 1, 2$), the positive linear combination (conical combination) $\alpha = \lambda_1 \alpha^1 + \lambda_2 \alpha^2$ verifies also the inequalities, which means that the set of those α 's form a convex (polyhedral) cone $\mathcal{K}$. To identify the cone we look for its extreme rays since any element of the convex cone is a positive (conical) combination of its extreme rays. There exist several methods to identify these extreme rays [1, 3, 4, 8].

One simple way to identify extreme rays is to consider the trace of $\mathcal{K}$ on the appropriate plane $\mathcal{P}$ determined by the condition

$$\text{sgn}(\alpha_1)\alpha_1 + \text{sgn}(\alpha_2)\alpha_2 + \text{sgn}(\alpha_3)\alpha_3 = 1, \quad (3)$$

and determine the extreme points of the convex polyhedron $\mathcal{P} \cap \mathcal{K}$. Moreover, let us observe that to any $\alpha \in \mathcal{K}$ and $\alpha \neq 0$, there exists a $\lambda > 0$ such that $\lambda\alpha \in \mathcal{P} \cap \mathcal{K}$.

For our problem the condition (3) is

$$\alpha_1 + \alpha_2 - \alpha_3 = 1.$$

To this equality, we add 2 inequalities among the 7 in (2) that we set as equalities, and we solve the 3×3 linear system. If its solution satisfies the remaining other inequalities in (2), then we have an extreme point of the polyhedron, so an extreme rays of the cone. For this example there are $\binom{7}{2} = 21$ such 3×3 linear systems to solve.

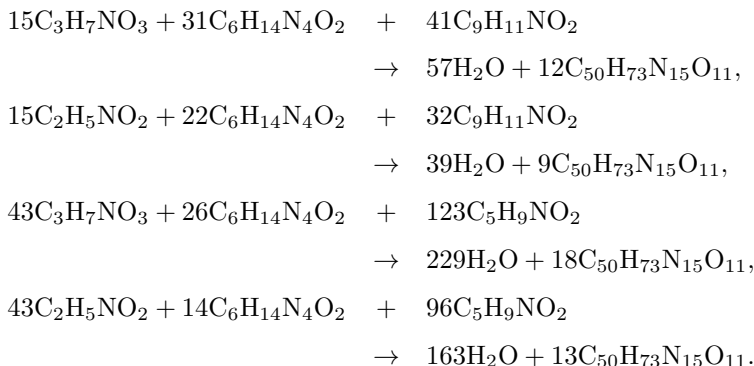
For our example we get the following 4 extreme points (everywhere we could remove the denominators)

$$\begin{cases} \alpha^1 &= (0, 41, -12)/53, \\ \alpha^2 &= (0, 32, -9)/41, \\ \alpha^3 &= (41, 0, -18)/59, \\ \alpha^4 &= (32, 0, -13)/45, \end{cases}$$

and

$$\begin{cases} X_1 = (0, -57, 15, 31, 0, 41, -12)/53, \\ X_2 = (15, -39, 0, 22, 0, 32, -9)/41, \\ X_3 = (0, -229, 43, 26, 123, 0, -18)/59, \\ X_4 = (43, -163, 0, 14, 96, 0, -13)/45, \end{cases}$$

and without considering the denominators, we have



Any conical combination of the X'_i 's produce a set of coefficients for balancing the chemical equation. Let us set $\Lambda = (\lambda_1, \lambda_2, \lambda_3, \lambda_4)$, and consider $\alpha = \sum_{i=1}^4 \lambda_i \alpha^i$, we get the following examples

$$\begin{cases} \Lambda'_5 = (106/41, 0, 649/1763, 45/43)/4, \\ \Lambda''_5 = (0, 41/16, 59/43, 45/688)/4, \\ \Lambda_6 = (0, 205/8, 236/43, 2025/344)/37, \\ \Lambda'_7 = (1113/41, 0, 15281/1763, 180/43)/40, \\ \Lambda''_7 = (9911/615, 164/15, 531/41, 0)/40, \end{cases}$$

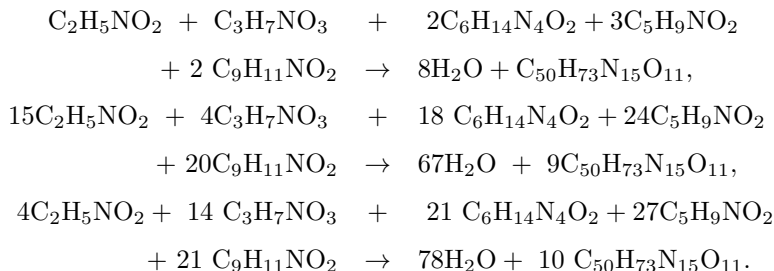
and

$$\begin{cases} \alpha^5 = (1, 2, -1)/4, \\ \alpha^5 = (1, 2, -1)/4, \\ \alpha^6 = (8, 20, -9)/37, \\ \alpha^7 = (9, 21, -10)/40, \\ \alpha^7 = (9, 21, -10)/40, \end{cases}$$

so

$$\begin{cases} X_5 &= (1, -8, 1, 2, 3, 2, -1)/4, \\ X_6 &= (15, -67, 4, 18, 24, 20, -9)/37, \\ X_7 &= (4, -78, 14, 21, 27, 21, -10)/40, \end{cases}$$

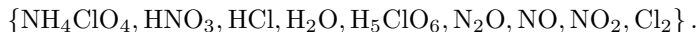
and we get the following balanced chemical equations



Remark. To slightly simplify the method we could remove the condition (3), and fix one of the α' 's at a nonzero value.

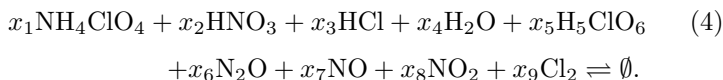
4 Second multi-parameter example

Let us consider a more complicated multi-parameter chemical equation [11], in the sense that the dimension of the null space is higher than in the preceding examples. The molecules of the reactions we look for are



4.1 Free sets of reactants and products

We look for x_i ($i = 1, \dots, 9$) such that



The coefficient matrix of this system is

$$\Sigma = \begin{bmatrix} \text{Cl} & : & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 2 \\ \text{H} & : & 4 & 1 & 1 & 2 & 5 & 0 & 0 & 0 & 0 \\ \text{N} & : & 1 & 1 & 0 & 0 & 0 & 2 & 1 & 1 & 0 \\ \text{O} & : & 4 & 3 & 0 & 1 & 6 & 1 & 1 & 2 & 0 \end{bmatrix}.$$

Its row reduced echelon form is

$$\text{RREF}(\Sigma) = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 1 & 1/4 & -1/4 & -3/2 \\ 0 & 1 & 0 & -1 & 0 & 1 & 3/4 & 5/4 & 3/2 \\ 0 & 0 & 1 & -1 & 0 & 0 & 1/8 & 3/8 & 13/4 \\ 0 & 0 & 0 & 0 & 1 & -1 & -3/8 & -1/8 & 1/4 \end{bmatrix}.$$

Using a permutation matrix Q on the column

$$Q = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

we get

$$\begin{aligned} \text{RREF}(\Sigma)Q &= \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 1 & 1/4 & -1/4 & -3/2 \\ 0 & 1 & 0 & 0 & -1 & 1 & 3/4 & 5/4 & 3/2 \\ 0 & 0 & 1 & 0 & -1 & 0 & 1/8 & 3/8 & 13/4 \\ 0 & 0 & 0 & 1 & 0 & -1 & -3/8 & -1/8 & 1/4 \end{bmatrix} \\ &= \begin{bmatrix} I_4 & N \end{bmatrix}. \end{aligned}$$

Since

$$\text{RREF}(\Sigma)Q \begin{bmatrix} -N \\ I_5 \end{bmatrix} = \begin{bmatrix} I_4 & N \end{bmatrix} \begin{bmatrix} -N \\ I_5 \end{bmatrix} = -I_4N + NI_5 = O,$$

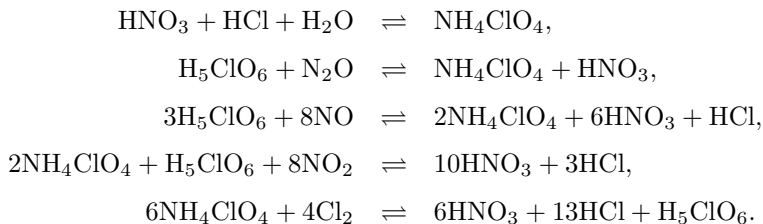
the columns of

$$Q \begin{bmatrix} -N \\ I_3 \end{bmatrix} = \begin{bmatrix} -1 & -1 & -1/4 & 1/4 & 3/2 \\ 1 & -1 & -3/4 & -5/4 & -3/2 \\ 1 & 0 & -1/8 & -3/8 & -13/4 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 3/8 & 1/8 & -1/4 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

form a basis for the null space of Σ . The dimension of the null space is 5, and a basis is the set

$$\left\{ \begin{pmatrix} -1, & 1, & 1, & 1, & 0, & 0, & 0, & 0, & 0 \end{pmatrix}, \right. \\ \left. \begin{pmatrix} -1, & -1, & 0, & 0, & 1, & 1, & 0, & 0, & 0 \end{pmatrix}, \right. \\ \left. \begin{pmatrix} -2, & -6, & -1, & 0, & 3, & 0, & 8, & 0, & 0 \end{pmatrix}, \right. \\ \left. \begin{pmatrix} 2, & -10, & -3, & 0, & 1, & 0, & 0, & 8, & 0 \end{pmatrix}, \right. \\ \left. \begin{pmatrix} 6, & -6, & -13, & 0, & -1, & 0, & 0, & 0, & 4 \end{pmatrix} \right\}.$$

The elements of this basis leads to the balanced equations



4.2 Fixed sets of reactants and products

Now let us fix the set of reactants and the set of products to be respectively

$$\{\text{NH}_4\text{ClO}_4, \text{HNO}_3, \text{HCl}, \text{H}_2\text{O}\} \text{ and } \{\text{H}_5\text{ClO}_6, \text{N}_2\text{O}, \text{NO}, \text{NO}_2, \text{Cl}_2\}.$$

So we want to balance (4) with $x_1 \geq 0$, $x_2 \geq 0$, $x_3 \geq 0$, $x_4 \geq 0$, $x_5 \leq 0$, $x_6 \leq 0$, $x_7 \leq 0$, $x_8 \leq 0$, and $x_9 \leq 0$.

We consider a linear combination of the elements of the basis of the null-space

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \\ x_8 \\ x_9 \end{bmatrix} = \alpha_1 \begin{bmatrix} -1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \alpha_2 \begin{bmatrix} -1 \\ -1 \\ 0 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \alpha_3 \begin{bmatrix} -2 \\ -6 \\ -1 \\ 0 \\ 3 \\ 0 \\ 8 \\ 0 \\ 0 \end{bmatrix} + \alpha_4 \begin{bmatrix} 2 \\ -10 \\ -3 \\ 0 \\ 1 \\ 0 \\ 0 \\ 8 \\ 0 \end{bmatrix} + \alpha_5 \begin{bmatrix} 6 \\ -6 \\ -13 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 4 \end{bmatrix},$$

and we get the following inequalities

$$\left\{ \begin{array}{lcl} x_1 & = & -\alpha_1 - \alpha_2 - 2\alpha_3 + 2\alpha_4 + 6\alpha_5 \geq 0, \\ x_2 & = & \alpha_1 - \alpha_2 - 6\alpha_3 - 10\alpha_4 - 6\alpha_5 \geq 0, \\ x_3 & = & \alpha_1 - \alpha_3 - 3\alpha_4 - 13\alpha_5 \geq 0, \\ x_4 & = & \alpha_1 \geq 0, \\ x_5 & = & \alpha_2 + 3\alpha_3 + \alpha_4 - \alpha_5 \leq 0, \\ x_6 & = & \alpha_2 \leq 0, \\ x_7 & = & 8\alpha_3 \leq 0, \\ x_8 & = & 8\alpha_4 \leq 0, \\ x_9 & = & 4\alpha_5 \leq 0. \end{array} \right. \quad (5)$$

We can remove the constraints on x_2 and x_3 , they will always be satisfied if the remaining constraints are satisfied. To solve the problem, we add the condition

$$\alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 - \alpha_5 = 1,$$

and proceed as we did in Section 4.

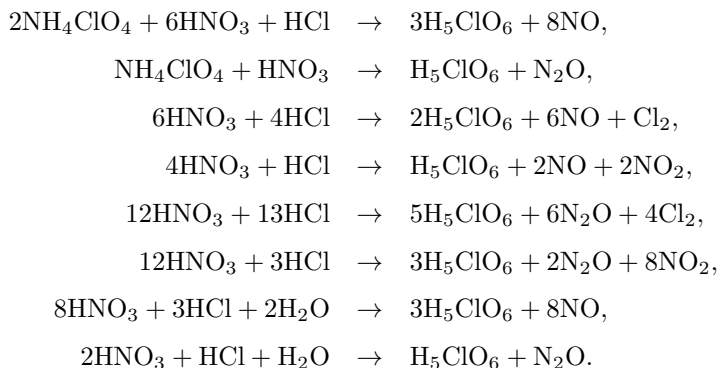
For this example we get the following 8 extreme points

$$\left\{ \begin{array}{lcl} \alpha^1 & = & (0, 0, -1, 0, 0), \\ \alpha^2 & = & (0, -1, 0, 0, 0), \\ \alpha^3 & = & (0, 0, -3, 0, -1)/4, \\ \alpha^4 & = & (0, 0, -1, -1, 0)/2, \\ \alpha^5 & = & (0, -6, 0, 0, -1)/7, \\ \alpha^6 & = & (0, -2, 0, -1, 0)/3, \\ \alpha^7 & = & (2, 0, -1, 0, 0)/3, \\ \alpha^8 & = & (1, -1, 0, 0, 0)/2, \end{array} \right.$$

and

$$\left\{ \begin{array}{lcl} X_1 & = & (2, 6, 1, 0, -3, 0, -8, 0, 0), \\ X_2 & = & (1, 1, 0, 0, -1, -1, 0, 0, 0), \\ X_3 & = & (0, 6, 4, 0, -2, 0, -6, 0, -1), \\ X_4 & = & 2(0, 4, 1, 0, -1, 0, -2, -2, 0), \\ X_5 & = & (0, 12, 13, 0, -5, -6, 0, 0, -4)/7, \\ X_6 & = & (0, 12, 3, 0, -3, -2, 0, -8, 0)/3, \\ X_7 & = & (0, 8, 3, 2, -3, 0, -8, 0, 0)/3, \\ X_8 & = & (0, 2, 1, 1, -1, -1, 0, 0, 0)/2, \end{array} \right.$$

and without considering the denominators, we have



Again any conical combination of the X'_i 's produce a set of coefficients for balancing the chemical equation.

Another method has been recently presented in [11]. It use monoid and Hilbert basis. It seems more complex, and they get 17 vectors in the Hilbert basis compared to 8 for our method on this example.

5 Conclusion

We have considered a general method to mathematically balance chemical equations which, in fact, is an occurrence of the well known vertex enumeration problem, which is a hard problem in computational geometry [1, 3, 4, 8]. Nothing assure that a mathematically balanced equation is observable. The method could be useful to suggest settings for experimentation. Adding inputs from chemistry could help to decrease the dimension of the null space and then simplify the problem.

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