# Mathematical Models of Reaction Mechanisms

a PhD - Thesis

*Dr. Szalkai István*

University of Veszprém, Department of Mathematics

# Contents

# Chapter 1

# Introduction

Mathematical formulation and even algorithmic approaches of finding minimal (direct) and overall *reactions and mechanisms* grew a great literature in the last two decade. We refer here only to the works of *Happel-Sellers-Otarod* [$HS83$], [$S84$], [$HOS90$], of *Pethő* [$P90$], [$P93$], [$P95$], of *Friedler-Bertók-Fan* [$B99$] , [$FBF00$], *Fishtik-Alexander-Datta* [$FAD99$], [$FD99$] , *Chevalier-Melenk-Warnatz* [$CMW90$], and of *LaFlamme* and the present author [$Sz91$], [$SzL95$], [$SzDL96$], [$Sz97$], [$SzL98$], [$Sz00$], [$Sz01$], [$SzDHL01$], [$Sz01a$], [$Sz01b$] and [$SzP01$] .

Further, recently many authors present lectures either on this field or on the applications of it, we mention here only some names as *X.X.Zhu* /Machaster, UK/, *Klára Hunek, Pál Jedlovszky* and *János Tóth* /Technical University, Budapest/, *Csanád* and *Botond Imreh* /University of Szeged/, *Gábor Kiss* and *Sándor Balogh* /MOL/.

Starting with our first paper on this field [$Sz91$] we followed the linear algebraic model of Pethő [$P90$], which was also invented independently by Happel-Sellers-Otarod [$HS83$] and in [$S84$] . In our further papers [$Sz91$], [$SzL95$], [$SzDL96$], [$Sz97$], [$SzL98$], [$Sz00$], [$Sz01$], [$SzDHL01$], [$Sz01a$], [$Sz01b$] and [$SzP01$] we made an extensive research of this field in several aspects.

In the present Thesis we introduce the main results of our research we made in the last decade[(1)] in the field of the theory of simplexes. This theory, among others can be applied to reaction mechanisms and other field of chemistry and physics, as reactions among species (or groups of atoms), dimensionless groups in physics, PNS networks, etc., too. These investiga-

[1)] Major parts of the researches was done during the author's study tour at **Professor Claude LaFlamme** in Calgary, Canada (1994) and at **Professor Árpád Pethő** in Hannover, Germany (1995).

tions do not deal with the same subject (simplexes) only: the questions and results have many connections among the different Chapters. One separate Chapter contains a list of further possible research questions, and another summarizes the basic definitions and properties of not common mathematical notions [matroids]. All the results collected in the present Thesis *have been appeared* in our papers [$Sz91$], [$SzL95$], [$SzDL96$], [$Sz97$], [$SzL98$], [$Sz00$], [$Sz01$] or are ready for preparation in manuscript form [$SzDHL01$], [$Sz01a$], [$Sz01b$] and [$SzP01$].

Let us now just to *outline* the content of our research contained in the present Thesis. A detailed Summary is given in the forthcoming Sections.

We introduce first our *mathematical model* (in Chapter 2) for describing and studying *reaction mechanisms among a given set of reactions.* The model is based in linear algebra only. This generality allows us to apply both the model and the algorithm based on it also for several other problems.

Next we present our polynomial fast *algorithm* for finding *all* minimal (circle-free) mechanisms in a given set of reactions based on our model. Let us mention that the presented algorithm, compared to others in the literature, is fully automatic, works for any input and is considerable fast.

Since the model we use is quite general, with (or without) some minor modifications of it and of the algorithm we can solve *other* related problems. For example, we can find also the *complete* set of (circle-free) reaction mechanisms resulting any *given* possible reaction, or all *reactions* which can occur as resulting reaction, i.e. containing terminal species only. These easy modifications can be carried out also for reactions, dimensionless groups or PNS networks.

A further Chapter is devoted to our *calculations* which give *upper and lower bounds* to the *number* of possible (circuit-free) mechanisms for any given set of reactions. These bounds are *sharp*, that is in some extreme cases the number of possible mechanisms is exactly the given small or large number. These bounds can be applied in any practical example for estimating the possible number of (cicuit-free) mechanisms, or in the other applications, the number of reactions, groups, etc. These calculations turn out more general than just in linear spaces, as our model required for reaction mechanisms. So, another Chapter deals with these more general calculations in the structure of *matroids.* (Since these structures might not be common for some Readers, in the last Chapter we provide a short introduction of them.)

This further generalization suggests still other applications. In Section "Beyond the thesis" we mention this and other questions which we suggest for further research.

Several *examples* for *applications* are presented in detail for explaining

both the model, the algorithm, its speed, its variations for other related problems and for comparing the number of outcomes to our calculations of (upper and lower) bounds.

Another but closely related question concerning reactions and mechanisms are the *quantities* which are *linear* on the set of reactions. (We call these quantities *valuation operators.*) A quantity is *linear* if its value for the final reaction can be computed from the values of those reactions which mechanisms results the final reaction, using just a linear computation. (The exact definition with a deep linear algebraic investigation is provided in Chapter 6 "The valuation operator".)

The below Sections provide more detailed summary of the results of the Thesis. The last one is devoted for acknowledgements.

## 1.1 Simplexes

For fully understanding of the generality of our method and algorithm we devote Chapter 2 "*Introduction and mathematical formulation*" for examples of different types (as *atoms, reactions, mechanisms, process network syntheses or dimensionless units in physics*) and the abstract general mathematical model for them. Shortly speaking, each object (reaction, mechanism, etc.) we represent by a vector in a suitable dimension in such a way that (chemical/linear) combination of these object are represented by the same linear combination of their vectors.

For example, any chemical speci (or group of atoms, i.e. functional bond only)

$$A = \sum_{i=1}^{m} a_i \cdot E_i \quad ,$$

consisting of the atoms $E_1, ..., E_m$ can be assigned to the vector

$$\mathbf{A} := [a_1, ..., a_m]^T$$

from the $m$ -dimensional linear space.

Or, to the reaction

$$X = \sum_{i=1}^{n} b_i \cdot \mathbf{A}_i \quad ,$$

which uses the species $A_1, ..., A_n$ $(b_i \in \mathbb{Z}$ for $i = 1, \ldots, n)$ we can correspond the vector

$$\mathbf{X} := [b_1, ..., b_n]^T \in \mathbb{R}^n \quad .$$

Though the mathematical notion ("*simplex*") we introduce has its own curiosity in mathematics, here we focus mainly on chemical aspects of its applications only.

Since this linear algebraic notion plays central role in the present Thesis, let its definition stay also here.

**Definition 1.1** *(see Def.2.1) A set of vectors $S \subset \mathbb{R}^n$ is called a* ***simplex*** *iff $S$ is linearly dependent but all of its proper subsets $T \subset S$ , $T \neq S$ are linearly independent.* □

In our applications vectors and simplexes may be interpreted in different ways in stoichiometry or in physics. For example, if we consider species / functional bonds / groups of atoms as vectors then simplexes determine *minimal reactions.* Second, in the case under *vectors* we mean reactions, each simplex gives us a *minimal / direct mechanisms.* Third, if phisical quantities (measuring) units are represented by vectors, simplexes mean dimensionless quantities (constant) built up from them by multiplication and division.

## 1.2 The algorithm

In Chapter 3 "*The algorithm*" we first introduce our new general algorithmic method for solving the general algebraic problem: to find all simplexes in a given (finite) set of vectors $H \subset \mathbb{R}^n$. In other terms, for example: it generates all minimal (circuit-free) reaction-mechanisms. This algorithm is based our above linear algebraic model, it lists all the simplexes in *polinomial* short time, without any repetition and is fully automatic.

It is clear (by the definition) that all simplexes in $\mathbb{R}^n$ must have size at most $n+1$ . However, there is no mean to try out *all* subsets of $H \subset \mathbb{R}^n$ having this or smaller size for finding all simplexes in $H$ : this would require

$$\sum_{i=1}^{n+1} \binom{M}{i} = \binom{M+1}{n+2} - 1 \approx (M+1)^{n+2} \tag{1.1}$$

steps where $M$ denotes the size of $H$ , the number of inputs, each if of dimension $n$ .

The base idea for accelerating our algorithm is the following Fact (which follows immediately from the definition of simplexes):

**Fact:** *No subset of a (linearly) independent set can be simplex, neither can any set which contains a dependent subset.* □

Our algorithm starts with the singleton containing the first element of $H$. After, in each step it modifies the (just investigated) candidate subset of $H$ : enlarges, decreases or replaces one element of it, according to that subset was dependent or independent and according to the previous Fact. This observation considerable accelerates the algorithm *in most of the cases*. Computer experiments, which are presented in Chapter 8 show that our algorithm is really considerably fast.

On the other hand, our results in Chapter 4 "*On the number of simplexes*" (or see in the next Section) show that in many *extreme cases* the (maximal) number of simplexes (outputs) may be exactly

$$\binom{M}{n+1} \approx M^{n+1} \tag{1.2}$$

which has just a bit smaller magnitude than (1.1). (In Chapter 4 we also provide *lower* bounds for the number of simplexes [outputs].) For comparison, in all computer examples in Chapter 8 we indicate both real running time (in seconds) and these lower and and upper bounds of possible extreme cases.

This (base) algorithm was first published in [$Sz91$] in 1991, it differs in its basis from Happel- Sellers- Otarod's in [$HOS90$] and Bertók's [$B99$].

Surprisingly enough only slight modifications were neccessary of the *input set* for many different and effective further applications.

For example, if only a set of reactions as possible parts of a mechanism and the set of terminal and nonterminal (chemical) compounds are given, we might be asked to find (all) the (possible) *resulting* reactions which contain of terminal compounds *only*. This requirement can be answered by an easy modification of the input matrix (and an unmodified run of the algorithm).

Or, we may want to collect those direct (circuit-free) mechanisms which lead to a certain (given) reaction. Since each reaction is represented by a vector and circuit-free mechanisms correspond to simplexes, we only have to look for simplexes which contain the vector representing our given reaction. For achieveing this we only have to analyse the method of our algorithm how it selects new sets (more precisely it modifies the old ones) for looking simplexes. We have just to put this given vector to the first place and to stop the algorithm when the investigated set leaves this first vector. Similar tricks are also applicable for more given vectors and various requirement for simplexes which contain *all* of them or *at least one* of them, etc.

Though there is no (theoretical or practical) limit for the number of the input-vectors or for their dimension for our algorithm, a previous decreasing of them, if applicable, is always useful. This question is discussed in Section 3.2.0, computer experiments are shown in Chapter 8.

These modifications are discussed in the second part of Chapter 3, in Sections 3.2.0 through 3.2.3. We conclude Chapter 3 with a mathematical justification of the correctness of these modifications of our algorithm.

These extensions of the base algorithm with their mathematical investigations have been appeared in [$Sz01$] .

## 1.3 On the number of simplexes

In Chapter 4 "*On the number of simplexes*" we present a detailed investigation on the number of simplexes and the *structure* of the extreme configurations. Let us highlight that the *maximal number* of simplexes would not be a hard combinatorial example (using Sperner's wellknown theorems from combinatorics), but we also reveal the *structure* of the extreme configurations, too, which is the hard problem.

In other words, for example, considering a (given) list of reactions, we can give numerical bounds for the number of circle-free mechanisms possible among these reactions.

In details, in Chapter 4 we prove the following results:

**Theorem 1.2** *(see Thm.4.3) For any $\mathcal{H} \subset \mathbb{R}^n$ of fixed size, so that $\mathcal{H}$ spans $\mathbb{R}^n$ , $simp(\mathcal{H})$ is maximal if and only if any $n$ vectors of $\mathcal{H}$ are linearly independent.* □

**Theorem 1.3** *(see Thm.4.5) For any $\mathcal{H} \subseteq \mathbb{R}^n$ of fixed size so that $\mathcal{H}$ spans $\mathbb{R}^n$, $simp(\mathcal{H})$ is minimal if $\mathcal{H}$ consists of $n$ linearly independent equivalence classes of sizes differing by at most one from each other, where each equivalence class is a set of parallel vectors.*

*In case $\mathcal{H}$ contains no simplexes of size at least 3, the minimal configuration is unique.* □

Let again draw the Reader's attention to the facts that the above results focus mainly on the *structure* of the extreme configurations. The *number* of simplexes is a corollary of these results:

**Corollary 1.4** *(see Cor.4.10) Let $\mathcal{H} \subseteq \mathbb{R}^n$ so that $\mathcal{H}$ spans $\mathbb{R}^n$ and $|\mathcal{H}| = m$. Then, writing $m = an + b$ where $0 \leq b < n$ , we have*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(\mathcal{H}) \leq \binom{m}{n+1}$$

*and the extreme values may be achieved only by the following unique configurations as*

***(i)*** *simp($\mathcal{H}$) is* ***maximal*** *if and only if any $n$ vectors of $\mathcal{H}$ are linearly independent,*

***(ii)*** *simp($\mathcal{H}$) is* ***minimal*** *if $\mathcal{H}$ consists of $n$ linearly independent equivalence classes of sizes differing by at most one from each other, where each equivalence class is a set of parallel vectors.*

*Especially, when $m$ is divisible by $n$ (i.e. $b = 0$), we have*

$$n \cdot \binom{\frac{m}{n}}{2} \leq simp(\mathcal{H}) \leq \binom{m}{n+1} \quad . \quad \square$$

The question for the minimum value of *simp*($\mathcal{H}$) is *open* if no parallel vectors are allowed in $\mathcal{H}$. Unfortunately our methods in proving the minimum case work only if we allow parallel vectors (ie. to use the same specie more than one time). So the lower bound must be much larger when we exclude parallel vectors, but at this time the question for the minimum value of *simp*($\mathcal{H}$) is open if no parallel vectors are allowed in $\mathcal{H}$ . (This restriction is irrelevant in the maximum case.)

The special case $n = 3$ when excluding parallel vectors is dealt in the next Theorem:

**Theorem 1.5** *(see Thm.4.11) For any $\mathcal{H} \subseteq \mathbb{R}^3$ of fixed size not equal to 3, 4 or 7 such that $\mathcal{H}$ spans $\mathbb{R}^3$ and contains* ***no*** *collinear vectors, simp($\mathcal{H}$) is minimal if and only if $\mathcal{H}$ is contained in two intersecting planes, one of which is of size 3; i.e. precisely when $\mathcal{H}$ contains three linearly independent vectors $\{u_1, u_2, u_3\}$, another vector $v$ coplanar with $u_1$ and $u_2$ and the rest $\mathcal{H}\backslash\{u_1, u_2, u_3, v\}$ coplanar with $u_2$ and $u_3$ .* $\square$

For $|\mathcal{H}| = 3$ , $\mathcal{H}$ must consist of 3 linearly independent vectors as it is required to span $\mathbb{R}^3$, and therefore $simp(\mathcal{H}) = 0$ . For $|\mathcal{H}| = 4$, there are 2 optimal configurations with 1 simplex. The optimal configurations are explained below in Figures 4.1 and 4.2 in the third Section of Chapter 4.

**Corollary 1.6** *(see Cor.4.12) Let $\mathcal{H} \subseteq \mathbb{R}^3$ such that $\mathcal{H}$ spans $\mathbb{R}^3$, $|\mathcal{H}| = m \geq 4$ and contains no collinear vectors. Then we have:*

$$\binom{m-2}{3} + 1 + \binom{m-3}{2} \leq simp(\mathcal{H}) \leq \binom{m}{4} \quad . \quad \square$$

These investigations throw some light also to the behaviour and speed of our algorithm, and also to all the applications as well. In other words, these formulas give immediately bounds for the *number* of chemical *minimal reactions / direct mechanisms* in a given set of *species* (groups of atoms or functional bonds) / *reactions* since the number of the involved elements/species is known and fixed.

Let us highlight here again that our bounds are sharp and we also characterize the unique extreme constructions. The only open case is when we do *not* allow parallel vectors is solved in only in $\mathbb{R}^3$ , the proof occupies the last Section of our Chapter 4. These results are originally published in our joint works [$SzL95$] , [$SzL98$] with Claude LaFlamme.

Higher dimensions are mentioned in Chapter **7** "*Beyond the thesis".*

## 1.4 Computational results

In Chapter 8 "*Computational results*" we present some runs of our base algorithm and of the extended variants of it. We used a PsII Packard Bell Personal Computer with 400 MHz CPU speed, the number and the dimension of the input vectors in our examples both are between 10 and 20. We used examples from the literature and compared our results (both output and speed) to the other algorithms mentioned in the literature.

From these in- and outputs and Tables not only the running time and the size of the input and output (one of them has more than 3000 output simplexes, i.e. circle-free mechanisms) can be studied, but also several other quantities which we investigated theoretically in the previous Chapters. These computational results have already been appeared in the last Section of [$Sz01$] .

## 1.5 Valuation operators

The other main question we deal with in the present Thesis is a theoretical investigation of linear quantities already used in chemistry.

Chapter 6 "*The valuation operator*" studies the behaviour of chemical species (functional bonds or just groups atoms) and reactions, mechanisms among them. Here we investigate the *linear* quantitative *characteristic* properties of the "*components*" taking part in a structure, in a reaction or in a mechanism. For example, the reaction heat of a reaction, resulted by a mechanism, can be computed from the reaction heats of the reactions taking part

of the mechanism. Further wellknown examples for linear (or additive) quantitatives of this kind are, for example *molar volumes*, *entalpy of formation* or *heat capacity* of species, the *standard Gibbs free energy change* (or free entalpy) of reactions, or *Reynold's number* of measure units in physics. Detailed examples and precise definitions are given at the introductory part of Chapter 6.

As a result of our linear algebraic interpretation, among others, a one-line proof for Hess' law is presented.

Our main results in this Chapter are first revealing the firm mathematical base of the concepts and methods already in use in this field of chemistry. (We use the wellknown results of higher linear algebra.) Second, we present new mathematical connections among these chemical concepts, which may offer new points of view or even new computing techniques for the linear characteristics of components.

The results of this Chapter have already been appeared in [$Sz00$].

## 1.6 Matroids

In Chapter 5 "*Matroids*" we investigate more general mathematical concept of vectors, simplexes, linear spaces and bases of them. Matroids are relatively new structures in mathematics, they are common generalization of *linear spaces* (considering only independence of vectors but not the operators), *graphs* (the structure of circle-free edge sets), *set-systems*, in other words *hypergraphs* (investigating the independence of certain subsets of a ground set), *partitions* of sets, etc. Matroids deal with the properties of the relation of *independence*, which means, in the language of mechanisms that a *mechanism* is *circuit-free*. The definition and basic properties of matroids is presented in the Appendix.

More precisely we focus on the generalization of the question on the *number* of bases and of circuits in matroids *and* on the *structure* of the extreme constructions. Similarly to the previous Chapter, we have to deal separately with the cases *with* and *without* loops and/or parallel elements.

The results in this Chapter are results of a joint research of several years with György Dósa, Mihály Hujter and Claude LaFlamme, are published in [$SzDL96$] and planned in [$SzDHL01$] .

In Chapter 5 we justify the results below:

**Theorem 1.7** *(see Thm.5.3) If* $m > n+1$ *, then only the uniform matroid* $U_{m,n}$ *contains the maximum number of circuits,* $\binom{n+1}{m}$ *. If* $m = n+1$ *, all matroids of size* $m$ *and of rank* $n$ *contain exactly 1 circuit.* $\square$

**Theorem 1.8** *(see Thm.5.5) Only the uniform matroid $U_{m,n}$ contains the maximum number of bases, namely $\binom{m}{n}$ .* □

**Theorem 1.9** *(see Thm.5.6) For each $m$ and $n$ there is a unique matroid $\mathcal{M}_o$ of size $m$ and of rank $n$ containing minimal number of bases, namely 1, when we allow loops in the matroid.* □

**Theorem 1.10** *(see Thm.5.7) Any matroid $\mathcal{M}$ of size $m$ and of rank $n$ contains at least $n-m$ circuits. A matroid contains exactly $m-n$ circuits if and only if the circuits of the matroid are pairwise disjoint.* □

**Theorem 1.11** *(see Thm.5.11) Suppose that there are neither large circuits nor loops in the matroid $\mathcal{M}$ and $\{a_1, a_2, \ldots, a_n\}$ is any fixed base of $\mathcal{M}$ . If $\vartheta_i$ denotes the number of elements in $\mathcal{M}$ parallel to $a_i$ (including $a_i$ itself) for $i = 1, 2, \ldots, n$ , then $\mathcal{M}$ contains the minimum number of circuits iff $|\vartheta_i - \vartheta_j| \leq 1$ for $i \neq j$ .* □

**Corollary 1.12** *(see Cor.5.12) The minimum number of circuits in a matroid of size $m$ and of rank $n$, where $m = an + b$ , $0 \leq b < n$ , is*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$$

*and in particular, if $m$ is a multiple of $n$,*

$$n \cdot \binom{\frac{m}{n}}{2} \quad . \quad \square$$

**Theorem 1.13** *(see Thm.5.13)* ***a)*** *For $m < 2n$ , a matroid of size $m$ and rank $n$ contains the minimal number of circuits iff all its circuits are disjoint.*

***b)*** *For $m \geq 2n$ , a matroid contains the minimal number of circuits iff it contains only 2-element circuits (i.e. parallel elements), and the sizes of the equivalence classes of parallel elements differ by at most 1 .* □

**Theorem 1.14** *(see Thm.5.19) A matroid $\mathcal{M}$ of size $m$ and rank $n$ contains the minimal number of bases iff it has a base $\{a_1, a_2, \ldots, a_n\}$ such that all other elements in $\mathcal{M}$ are parallel to $a_1$ .* □

**Corollary 1.15** *(see Cor.5.21) The minimal number of bases is $m-n+1$ , and the minimal configuration is unique when we allow no loops but parallel elements in the matroid.* □

## 1.7 Beyond

In Chapter 7 "*Beyond the Thesis*" we just list, in a more or less detailed form, a couple of open questions and ideas, connected to the fields of the thesis, for further researches. We indicate that the investigation of most of these questions are in progress and are to be published in the near future in $[Sz01a]$ , $[Sz01b]$ and in $[SzP01]$ .

Among others, we formulate the below problems.

**Problem 1.16** *(see Probl.7.3) What is the minimal number of simplexes if assuming the minimal size of dependent subsets ('circles' in matroids) is at least $k$ for any fixed $k \in \mathbb{N}$ ?* $\square$

**Conjecture 1.17** *(see Conj.7.2) Suppose that $\mathcal{H}$ is of fixed size, spans $\mathbb{R}^n$ and contains **no** collinear vectors. Then the minimal value of $simp(\mathcal{H})$ is is attained precisely in the following configurations:*

***1.*** *If $n$ is even, $\mathcal{H}$ contains $n$ linearly independent vectors $\{u_i : i = 1, \dots, n\}$ and the remaining ones are divided as evenly as possible between the planes $\{[u_i, u_{i+1}] : i = 1, 3, \dots, n-1\}$ .*

***2.*** *If $n$ is odd, $\mathcal{H}$ again contains $n$ linearly independent vectors $\{u_i : i = 1, \dots, n\}$, one extra vector in the plane $[u_{n-1}, u_n]$ and finally the remaining vectors divided as evenly as possible between the planes $\{[u_i, u_{i+1}] : i = 1, 3, \dots, n-2\}$ with lower indices having precedence.* $\square$

**Conjecture 1.18** *(see Conj.7.4) For matroids $\mathcal{M}$ of size $m$ and with rank $k$ , minimal number of circuits is contained in the uniform matroid $U_{k,n-3}$, so the lower bound is*

$$1 + 3 \cdot \binom{m-3}{k-1} + 3 \cdot \binom{m-3}{k-2} + \binom{m-3}{k-3} \leq simp(\mathcal{M}) \quad . \qquad \square$$

**Problem 1.19** *(see Probl.7.5) Let the set of vectors $H := \{A_1, ..., A_m\} \subset \mathbb{R}^N$ and a subset of $H$ $V := \{V_1, \dots, V_t\} \subset H$ be given. What is the possible minimal and maximal number of simplexes $S \subset H$ containing at least one vector from the set $V$ , that is $S \cap V \neq \emptyset$ ?* $\square$

**Definition 1.20** *(see Def.7.6) Let the vectors of the $i$ 'th hierarchy ($i \in \mathbb{N}$) be*

$$H_i := \{A_1^{(i)}, ..., A_{k_i}^{(i)}\} \subset \mathbb{R}^{n_i} \quad .$$

*Suppose, that the set of simplexes of $H_i$ is*

$$\mathcal{S}_i := \{S_1^{(i)}, ..., S_{t_i}^{(i)}\} \subseteq \mathcal{P}(H_i)$$

*and identify these simplexes to the set of indices*

$$S_j^i := \{u \leq k_i : A_u \in S_j^i\} \quad \subseteq \{1, ..., k_i\} \ , \quad (j \leq t_i) \quad .$$

*Suppose further that these simplexes determine (up to a constant factor) the linear combinations*

$$\sum_{v \in S_j^i} \lambda_v^{i,j} A_v = \underline{0} \qquad (j \leq t_i).$$

*Then we define the vectors of the* ***next hierarchy*** *as*

$$A_j^{(i+1)} := [\mu_1, ..., \mu_{k_i}] \quad \in \mathbb{R}^{k_i} \ , \quad (j \leq t_i) \ ,$$

*where*

$$\mu_v = \begin{cases} \lambda_v^{i,j} & \text{if } v \in S_j^i \\ 0 & \text{if } v \notin S_j^i \end{cases} \ ,$$

*so, of course, the next dimension is*

$$n_{i+1} = k_i \quad . \qquad \square$$

**Problem 1.21** *(see Probl.7.7) Study the properties of this hierarchy, the connections among these levels, and study their applications to linear algebra, chemistry, physics, etc.* $\square$

**Problem 1.22** *(see Probl.7.9) Is there a (finite) set of circuit-free mechanisms/reactions which linear combinations would give the set of all mechanism/reactions?*

*Find this set theoretically, algorithmically, and/or describe its properties.* $\square$

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# Chapter 2

# Examples and mathematical formulation

The mathematical model we use in the present Thesis is standard and quite wellknown, first described in [$P90$] and [$Sz91$], partly similar to Seller's and others' [$S84$], [$HOS90$]. By "standard" we mean that linear algebraic representation of reactions and their mechanisms is used in most of the works published in the theory of reaction mechanisms. Well, if we consider the law of mass balance (conservation of material) only, neglecting the *reasons* of a mechanism, this method is easy and quite natural.

Following Á.Pethő, we extend the use of our linear algebraic model for other fields. Let us highlight in advance that our method is exactly the *same* both for *reactions, mechanisms,* and for *dimensionless groups.* We can describe all of these problems in the language of linear combinations of vectors, and in order to find the desired object (minimal reactions/mechanisms/dimensionless groups) we need to find, in all of the three above cases, minimal *linearly dependent* subsets of these vectors. We call these subsets of vectors *simplexes.* Since our algorithm finds *all* simplexes in *any* set of given vectors, it can be applied immediately for all of the three problems above.

Let us start with some examples to which we will be able to use our general linear algebraic concepts and our proposed algorithmic solution. These examples help us to deduce and understand the general notions we have to deal with.

## 2.1 Reactions

If we are given the chemical species (or groups of atoms, i.e. functional bonds only) $A_1, ..., A_n$ which consist of the atoms $E_1, ..., E_m$ as

$$A_j = \sum_{i=1}^{m} a_{i,j} \cdot E_i$$

where $a_{i,j} \in \mathbb{N}$ for $j = 1, ..., n$ and $i = 1, ..., m$, and we suppose that the sets $\{A_1, ...A_n\}$ and $\{E_1, ..., E_m\}$ are fixed, then we can *assign* the specie $A_j$ to the vector

$$\mathbf{A}_j := [a_{1,j}, ..., a_{m,j}]^T$$

for $j = 1, ..., n$, which vectors are elements of the $m$ -dimensional linear space spanned by the (natural) set of base vectors $\{E_1, ..., E_m\}$ .[(1)] We can of course assume that the vectors $A_j$ are, in fact, in the linear space $\mathbb{R}^m$, that is $A_j \in \mathbb{R}^m$ for $j = 1, ..., n$ .

Now, a (possible) chemical **reaction** among the species $\{A_j : j \in S\}$ does exists for any set of indices $S \subseteq \{1, ..., n\}$ *if and only if* the system of homogen linear equations

$$\sum_{j \in S} x_j \cdot \mathbf{A}_j = \mathbf{0} \tag{2.1}$$

has nontrivial solution for $x_j \in \mathbb{R}$ $(j \in S)$ by the law of mass balance (conservation of material). Further, a solution $\{x_j : j \in S\}$ easily determines uniquely a chemical reaction among the species $\{A_j : j \in S\}$ [(2),(3)] .

(The structure of the solutions of homogen linear equations is discussed in [*P*67].)

For example, consider the species $\mathbf{A}_1 = C$ , $\mathbf{A}_2 = O$ , $\mathbf{A}_3 = CO$ and $\mathbf{A}_4 = CO_2$ , that is we use the elements $E_1 = C$ and $E_2 = O$ as base "vectors". So $m = 2$ (=the number of atoms =the dimension) and

[1)] Of course the chemical speci $A_j$ and the vector $\mathbf{A}_j \in \mathbb{R}^m$ are not the same, above we mentioned the (natural) correspondence among them. However, in what follows, we will not emphasize the difference between the species $A_j$ and the vectors $\mathbf{A}_j \in \mathbb{R}^m$ .

[2)] Species (groups of atoms or functional bonds) with positive coefficients represent the right hand side of the reaction equality (starting compounds) while species with negative coefficients are moved to the left hand side (the products of the reaction).

[3)] All the solutions for the unknowns $x_j$ for $j \in S$ are rational since the components $a_{i,j}$ of the vectors $A_j$ — the coefficients of the homogen linear equation (0) — are all integers.

$n = 4$ (=the number of species/ vectors). The columns of the following Table represent the vectors $\mathbf{A}_1$ through $\mathbf{A}_4$ :

| | $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|---|
| C | 1 | 0 | 1 | 1 |
| O | 0 | 1 | 1 | 2 |
| | C | O | CO | $CO_2$ |

(2.2)

Now, for example, taking the $S = \{A_1, A_2, A_3\}$ we get the solution[4)]

$$X_1 = [x_1, x_2, x_3, x_4]^T = [1, 1, -1, 0]^T$$

which corresponds to the minimal reaction

$$C + O = CO \ .$$

The assumption that the equation (2.1) *has* nontrivial solutions is equivalent to that the vector set $\{A_j : j \in S\} \subseteq \mathbb{R}^m$ is *linearly dependent.* The corresponding reaction is called **minimal** iff for *no* $T \subset S, T \neq S$ there might be any reaction among the species $\{A_j : j \in T\}$ . That is, the vectorset $\{A_j : j \in T\}$ is *linearly independent* for any $T \subset S$ , $T \neq S$ .

This motivates Definition 2.1 below, where we will call such subsets of $\mathbb{R}^m$ as *simplexes.*

The only simplexes in the above example are (we write the sub-indexes of the vectors $A_i$ only) $S_1 = \{1, 2, 3\}$ , $S_2 = \{1, 2, 4\}$ , $S_3 = \{1, 3, 4\}$ and $S_4 = \{2, 3, 4\}$ . After solving the corresponding equations (2.1) we get the following (complete) list of minimal reactions :

$$\begin{array}{lcl} X_1 = [1, 1, -1, 0]^T & : & C + O = CO \\ X_2 = [1, 2, 0, -1]^T & : & C + O_2 = CO_2 \\ X_3 = [1, 0, -2, 1]^T & : & C + CO_2 = 2CO \\ X_4 = [0, 1, 1, -1]^T & : & O + CO = CO_2 \end{array} \tag{2.3}$$

(We continue *this* example in the next Section.)

Of course the reactions obtained in the above way are only possibilities, for example the reaction

$$2Au + 6HCl \rightarrow 2AuCl_3 + 3H_2$$

does not occur under normal conditions, i.e. we are interested in reactions from mathematical (quantitative) point of view.

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[4)] the co-ordinates of $X$ , corresponding to vectors $A_j$ which do NOT belong to the simplex $S$ , are always 0 .

## 2.2 Mechanisms

We can build up **mechanisms** (and also *minimal* ones) from any set of reactions just on the same way as we built up reactions from species in the previous Section. (Mechanisms are the main topic of our present research, we investigate them in more detail in Chapter 3 "*The algorithm and its variations*" and in Chapter 8 "*Computing results*".)

Well, if we are given the reactions $X_1, ..., X_k$ which use the species (groups of atoms or functional bonds) $A_1, ..., A_n$ then we can correspond these reactions to the vectors $\mathbf{X}_1, ..., \mathbf{X}_k \in \mathbb{R}^n$ in the $n$ -dimensional linear space $\mathbb{R}^n$, where the base vectors are $\mathbf{A}_1, ..., \mathbf{A}_n$ (=the standard base) representing each speci involved in the reactions. That is:

$$\mathbf{X}_j = \sum_{i=1}^{n} b_{i,,j} \cdot \mathbf{A}_i$$

where $b_{i,j} \in \mathbb{Z}$ for $j = 1, ..., k$ and $i = 1, \dots, n$ [5),6)].

Then *any* linear combination

$$\mathcal{M} = \sum_{j=1}^{k} \lambda_j \cdot \mathbf{X}_j \tag{2.4}$$

of the vectors $X_j$ with integer (or rational[7)]) coefficients $\lambda_j \in \mathbb{Z}$ represent a (possible) *mechanism* $\mathcal{M}$ in a natural way: during that mechanism the reaction $X_j$ takes place $\lambda_j$-many times (see the example below). Negative coefficients of course, mean that the corresponding reactions take place in reversed order. This reaction uniquely can be described by the vector of the coefficients

$$\underline{\lambda} := [\lambda_1, \dots, \lambda_k]^T \in \mathbb{Z}^k$$

Let us emphasize here that the detailed flow of the mechanism can be detected from the above vector of the coefficients *but* not at all from the sum-vector of the linear combination in (2.4).

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5) Moving the terms with negative coefficients $b_{i,j} < 0$ to the left-hand side of the equality (initial materials of the reaction) and leaving the others in the right-hand side (resulting materials) we get the usual form $\sum_{i \in X} b'_{i,j} A_i = \sum_{i \in Y} b'_{i,j} A_i$ of the mechanism.

6) by the law of the mass-balance we surely must have $\mathbf{AX} = \mathbf{0}$ for the matrix $\mathbf{A} := [A_1, ..., A_n]$ which "codes" the sum-formulae of the species $A_1, ..., A_n$ .

7) after multiplying all the coefficients by the common denominator we get integer coefficients

For further investigations we are adviced to extract the notion of the **resulting** (**overall**) **reaction** denoted by $\mathcal{R}(\mathcal{M})$ or $\mathcal{R}(\underline{\lambda})$ , corresponding to the mechanism $\mathcal{M}$ in (2.4) as :

$$\mathcal{R}(\underline{\lambda}) := \sum_{j=1}^{k} \lambda_j \mathbf{X}_j \qquad \in \mathbb{R}^n$$

(see [$S84$]) which is the final reaction, caused by the reactions $\mathbf{X}_j$ , $\lambda_j$ -many times one after another, $1 \leq j \leq k$ .

Let us remark that this model does not reveals the *order* of or any other connection among the reactions in a mechanism. B.Bertók recently introduced a graph -theoretical approach in [$B99$] for dealing with problem.

In the practice we distinguish *terminal species* (the starting and final ones that we interested in) and *intermediate* ones (which occur only during the mechanism). These terms are from [$HOS90$], the terms *chemical* and *active species* are also in use. According to this distinction of species (or just groups of atoms/ functional bonds), mechanisms are called **steady state mechanisms** ([$HS83$]) if the corresponding reaction (called **overall reaction**) contains of terminal (chemical) species only.

The mechanism is called **direct** or **minimal mechanism** ([$HS83$]) if the set of active reactions (vectors with nonzero coefficient)

$$S(\underline{\lambda}) := \{j \leq k \mid \lambda_j \neq 0\}$$

can not be decreased to yield the same resulting (overall) reaction $\mathcal{R}(\underline{\lambda})$. In other words: there is *no proper* subset $S' \subsetneqq S(\underline{\lambda})$ such that $\mathcal{R}(\underline{\mu}) = \alpha \cdot \mathcal{R}(\underline{\lambda})$ and $S(\underline{\mu}) = S'$ for some coefficient-vector $\underline{\mu} \in \mathbb{Z}^k$ and rational number $\alpha \in \mathbb{Q}$ . In this case the corresponding reaction $\mathcal{R}(\underline{\lambda})$ is called **simple** or **minimal reaction.**

Using our terminology, the solutions of the linear equations

$$\sum_{j \in S} y_j \mathbf{X}_j = \mathbf{0} \tag{2.5}$$

are minimal mechanisms *iff* the set $S \subseteq \{1, \ldots, k\}$ is a *simplex*, again !

Milner uses the term **direct path** and Sellers ([$S84$]) the **cycle-free mechanism** for minimal mechanisms.

With slight modifications of our pure linear algebraic algorithm, detailed in Chapter 3, we can solve several problems: we can find all minimal mechanisms resulting to any given reaction, or we can find all overall reactions if

the sets of terminal and intermediate (chemical and active) species are given. These and other applications are explained in detail in Section 3.2.

Happel, Sellers and Otarod in [$HOS90$] and Bertók in [$B99$] published algorithms for finding direct steady -state mechanisms Pethő and Kumar in [$KP85$] presented only an output for minimal reactions. Our computational results are listed and the related ones are compared to the above ones in Chapter 8 "*Computational results*".

Continuing our example from the previos Section, the co-ordinates of the vectors $\mathbf{X}_1, ..., \mathbf{X}_4$ , which represent the [minimal] reactions from , see (2.2) and (2.3), are

$$\begin{array}{l|cccc} & \mathbf{X}_1 & \mathbf{X}_2 & \mathbf{X}_3 & \mathbf{X}_4 \\ \hline \mathbf{A}_1 = C & 1 & 1 & 0 & 1 \\ \mathbf{A}_2 = O & 1 & 2 & 1 & 0 \\ \mathbf{A}_3 = CO & -1 & 0 & 1 & -2 \\ \mathbf{A}_4 = CO_2 & 0 & -1 & -1 & 1 \end{array} \tag{2.6}$$

Funny enough in our example we have again *four* simplexes. Solving the corresponding equations, we get the following list of minimal mechanisms (cycles):

$$\begin{array}{lrcl} Y_1 = [-1,0,1,1]^T : & C + O & \longleftarrow & CO \\ & O + CO & \longrightarrow & CO_2 \\ & C + CO_2 & \longrightarrow & 2CO \\ \\ Y_2 = [-1,1,-1,0]^T : & C + O & \longleftarrow & CO \\ & C + 2O & \longrightarrow & CO_2 \\ & O + CO & \longleftarrow & CO_2 \\ \\ Y_3 = [2,-1,0,-1]^T : & 2(C + O & \longrightarrow & CO) \\ & C + 2O & \longleftarrow & CO_2 \\ & C + CO_2 & \longleftarrow & 2CO \\ \\ Y_4 = [0,-1,2,1]^T : & C + 2O & \longleftarrow & CO_2 \\ & 2(O + CO & \longrightarrow & CO_2) \\ & C + CO_2 & \longrightarrow & 2CO \end{array} \tag{2.7}$$

For all these mechanisms $Y_i$ the resulting (overall) reaction $\mathcal{R}(Y_i) = 0$ (the void reaction) for $i = 1, 2, 3, 4$.

## 2.3 Dimensionless groups

This application was first mentioned in [*P*90] and is not from stoichiometry, but reveals the structure of composite measure units in physics, too: we can easily (fully automatically) find minimal identities among physical quantities by finding (all) simplexes again in a certain set of vectors.

Let there be given $m$ *elementary* quantities (mass,lenght,time,etc.) denoted by $E_1, ..., E_m$ and $n$ quantities $A_1, ..., A_n$ ($n \in \mathbb{N}$ is any number) as

$$A_j = \prod_{i=1}^{m} E_i^{a_{i,j}}$$

where $a_{i,j} \in \mathbb{Z}$ for $j = 1, ..., n$ and $i = 1, ..., m$ . Clearly we can *assign* the quantities $A_j$ to the vectors

$$\mathbf{A}_j := [a_{1,j}, ..., a_{m,j}]^T \in \mathbb{R}^m$$

for $j = 1, ..., n$, which vectors are in the $m$ -dimensional linear space $\mathbb{R}^m$. Now, a (possible) **dimensionless group** (real number) of the quantities $\{A_j : j \in S\}$ does exists for any $S \subseteq \{1, ..., n\}$ *iff* the equality

$$\prod_{j \in S} A_j^{x_j} = 1 \tag{2.8}$$

holds, or equivalently (considering the exponents) the homogeneous system of linear equations

$$\sum_{j \in S} x_j \cdot A_j = \mathbf{0}$$

has nontrivial solution for $x_j \in \mathbb{R}$ ($j \in S$) . That is, we again reached to the system of linear homogen equations (2.1) and to the problem of finding simplexes!

For example, consider the flow of a fluid through a heated tube and the heat transfer between the pipe wall and the fluid. Consider now the following quantities:

| | | | | | |
|---|---|---|---|---|---|
| $A_1$ | = | tube diameter | = $d$ | $(\ell)$ | (length, basic quantity) |
| $A_2$ | = | linear velocity | = $v$ | $(s/t)$ | |
| $A_3$ | = | fluid density | = $\rho$ | $(m/\ell^3)$ | |
| $A_4$ | = | viscosity | = $\nu$ | $(m/\ell t)$ | |
| $A_5$ | = | heat capacity | = $\kappa$ | $(A/t^2T)$ | |
| $A_6$ | = | heat transfer coeff. | = $\lambda$ | $(m/t^3T)$ | |
| $A_7$ | = | thermal conductivity | = $\mu$ | $(m\ell/t^3T)$ | |

In matrix form:

$$\begin{array}{l|cccc} & m & \ell & t & T \\ \hline \mathbf{A}_1 = d & 0 & 1 & 0 & 0 \\ \mathbf{A}_2 = v & 0 & 1 & -1 & 0 \\ \mathbf{A}_3 = \rho & 1 & -3 & 0 & 0 \\ \mathbf{A}_4 = \nu & 1 & -1 & -1 & 0 \\ \mathbf{A}_5 = \varkappa & 0 & 2 & -2 & -1 \\ \mathbf{A}_6 = \lambda & 1 & 0 & -3 & -1 \\ \mathbf{A}_7 = \mu & 1 & 1 & -3 & -1 \end{array} \tag{2.9}$$

For example, one minimal dimensionless group $X_1$ of the seven ones is the following:

$$X_1 = [0, 0, 0, 1, 1, 0, -1]^T,$$

which corresponds to the equality

$$\nu \cdot \kappa = \mu \cdot c$$

for some constant $c \in \mathbb{R}$ .

## 2.4 General formulation and remarks

From the above examples we can extract the following general linear algebraic notion (see [$P90$], [$Sz91$] or [$SzL95$]):

**Definition 2.1** *A set of vectors $S \subseteq \mathbb{R}^n$ is called a **simplex** iff $S$ is linearly dependent but all of its proper subsets $T \subset S$ , $T \neq S$ are linearly independent.* □

Let us point out that the above definition is a pure linear algebraic one, free of any chemical or physical meaning. Further, though it has some correlation with geometrical simplexes (see eg. [$Sz99$]), we should not mix the above definition with geometric simplexes.

On the other hand, general methods for looking for simplexes in a given set of vectors have many practical applications as we have seen in the previous Sections. For example, we could list all (possible) reactions among a given

set of species (or groups of atoms), or all (possible) mechanisms if the set of reactions we can use is given, etc.

Our two main question we deal in general in the present Thesis are the following. (1) - to invent an algorithm which searches for *all* simplexes in a given arbitrary set of vectors, and (2) - to give bounds for the number of simplexes which may be contained in a given arbitrary set of vectors, in advance (i.e. before we run the algorithm).

In what follows we state these problems in some more details.

As we have seen in the three introductory different examples in the above Sections, our first main mathematical problem is the following.

**Problem 2.2** *Find in a given vectorset* $H = \{v_1, v_2, \dots, v_M\} \subset \mathbb{R}^N$ *all simplexes* $S \subseteq H$ , *i.e. minimal dependent subsets of* $H$.

The author's **algorithm**, introduced already in 1991 in [$Sz91$] (and described in the next Chapter) solves directly the above computational problem, so can be applied directly for any of the three above practical problems. With some minor modifications we apply it for some other special questions, mainly in study of reaction mechanisms in Section 3.2. (See also [$Sz01$] .) We compare this algorithm to the others we found in the literature also in the next Chapter.

The second problem we focus on in the present Thesis is the *number* of simplexes in a given set of vectors (in other words, the number of the possible minimal mechanisms/ reactions).

**Problem 2.3** *Give upper and lower bounds for the number of simplexes which can be contained in a given set of vectors* $H \subset \mathbb{R}^N$ .

This question is partially solved yet, hard in full details. Our recent papers [$SzL95$] and [$SzL98$] give almost full answers. We present these results in Chapter 4 "*On the number of simplexes*".

Let us remark here that the *size* of the simplexes need *not* be the same, moreover they do not have any connection with the bases of the linear space (of all possible reactions/ mechanisms/ dimensionless groups). Examples in Chapter 8 show that large sets of vectors in high dimension might have few simplexes only, and small sets in low dimension might have many simplexes. This means, that it is very hard to give the *exact* number of simplexes in a given vectorset!

Beyond these two main questions we also introduce the results of our research on the generalizations of the above (second) problem.

The paper [$SzDHL01$] generalizes the mathematical notion of simplexes and counts their number not only in linear spaces but in more *general structures* called *matroids*. Matroids are common generalizations of linear spaces (or just certain sets of vectors), graphs, set systems, partitions, etc. This means, that any result we receive about the simplexes (circles) of matroids are direct results, among others for example, to linear spaces and so reactions mechanisms. (The definition and basic properties of matroids are introduced shortly in the last Chapter "*Appendix*".)

One could observe the connection between species and reactions (see (2.2), (2.3) and (2.4): the vectors of the higher "hierarchy" are the outputs of the hierarchy of a lower level. That is, the first three levels of this **hierarchies** are: **(1)** vectors (species/ groups of atoms/ functional bonds); **(2)** solution vectors corresponding to simplexes (i.e. reactions); **(3)** solution vectors of simplexes of the above vectorset (i.e. mechanisms in our example), **and so on ...!** Details and further properties of this *infinite* hierarchy will be investigated in [$Sz01a$] and [$SzP01$] . We discuss these hierarchies, among others, in Chapter 7 "*Beyond the thesis*".

A general linear algebraic notion (linear functional) is applied to chemical rections and mechanisms in [$P95$] where it is called the *valuation operator*, this question is investigated in our paper [$Sz00$], i.e. in Chapter 6 "*The valuation operator*".

This general notion and its linar algebraic investigation, of course, provides *another information, a developped one,* on reaction mechanisms and other chemical and physical phenomena. We deal not only with the possibility or the number of reactions but with their quantitaive characteristics. These kind of characteristics (we call them *valuation operators* in Chapter 6) are, for example the reaction heat, molar volumes, entalpy of formation or heat capacity of species, the standard Gibbs free energy change (or free entalpy) of reactions, or Reynold's number of measure units in physics.

**Problem 2.4** *Investigate the general properties of valuation operators in linear spaces.*

As we indicated above, this problem is dealt with in Chapter 6.

Further problems for further research which are connected to the present Thesis are listed in Chapter 7 "*Beyond the thesis*".

We conclude *this Section* with some general properties of simplexes. We will use them in our proofs in the forthcoming Chapters, but they are of interest of their own, too.

As prof. Árpád Pethő in [*P*67] showes, *all* solutions (not only minimals) of systems of homogeneous linear equations (2.1) can be calculated from minimal ones, this was the first case when he introduced the notion of simplexes.

Let us mention further that solving the system of linear equations (2.1) the solution vector can be assumed to have integer co-ordinates (components) only since (2.1) has integer coefficients, and we can multiply the rational components of the solution vector by the common denominator.

The following property is of interest in hiw own, but we will use it in the next Chapter when proving the equivalence of two variants of our algorithm.

**Lemma 2.5** *Any set of vectors* $U = \{u_1, \dots, u_m, v\}$ *is a simplex if and only if the set* $\{u_1, \dots, u_m\}$ *is linearly independent and all the coefficients* $\alpha_i$ *in the existing equality*

$$\mathbf{v} = \sum_{i=1}^{m} \alpha_i u_i \tag{2.10}$$

*are different from zero.*

**Proof.** If the set $U \backslash \{u_{io}\}$ would be dependent for some $i_0 \leq m$ then we would have

$$\beta_v \cdot \mathbf{v} + \sum_{i \neq io} \beta_i u_i = \mathbf{0}$$

and $\beta_v \neq 0$ since the set $\{u_1, \dots, u_m\}$ was assumed to be linearly independent.

This implies

$$\mathbf{v} = \sum_{i \neq io} \frac{\beta_i}{\beta_v} u_i$$

which contradicts to (2.10) since the coefficient of $u_{io}$ in the last linear combination is 0 while all the coefficients of $u_i$ for each $i \leq m$ constructing $v$ are unique since the set $\{u_1, \dots, u_m\}$ is assumed to be linearly independent.

■

# Chapter 3

# The algorithm and its variations

As we have indicated in the previous Chapters, our general linear algebraic algorithm, published in [$Sz91$] solves the mathematical Problem 2.2 in general. That is, it searches for all simplexes in an arbitrary (finite) collection of vectors $H \subset \mathbb{R}^n$ . On the basis of the examples in the previous Chapter, one can easily apply this algorithm directly for finding minimal either reactions, mechanisms or dimensionless groups.

The running time of the algorithm is *polynomial* in the size of the input, we discuss the speed of it just after we introduced our algorithm in the first Section in detail. A working program list in Pascal language of the main part of the algorithm is enclosed at the end of the present Chapter.

In the second Section we discuss a couple of "modifications" of our base algorithm for solving other related questions (mainly for studying mechanisms). Under these "modifications" of our algorithm we mean that for solving other related problems, we have to (and can) find the suitable form for input for solving those other problems. According to this trick, we can use our original algorithm (which searches all the simplexes in a given set of vectors) *without any modification*. The correctness of these modifications is proved in precise mathematical way in that and the subsequent Sections.

We compare our algorithm to others in the literature in the last Section of the present Chapter.

Many practical computer experiments are discussed in Chapter 8 "*Computational results*".

## 3.1 The algorithm

To start with we are given a set of vectors $H \subseteq \mathbb{R}^n$ (input) having size $|H| = M$ and we have to find *all* simplexes $S \subseteq H$, i.e. minimal dependent subsets of $H$, *without any repetition*, and in the *shortest time,* as possible.

The only interesting part of the algorithm might be how to generate (=book- keeping + modifying) all *simplexes* of a given set of vectors, since checking whether a chosen set of vectors is simplex or not is standard.

We chosed the lexicographic enumeration of all (possible) simplexes (subsets) and the "back- and forth" method for modifying. To store the elements of a subset $S \subsetneqq H$ of vectors $H$ (or equivalently the *indexes* of the vectors) we chose a string called **szimplex**[] in our program with an information-character on the last byte of it. (We put the info character to the last position only for convenience. Also for convenience we labeled the vectors with the characters A,B,... .)

The last info character of this string (representing the subset $S \subsetneqq H$ we just examine for being simplex) is one of the following:

| | |
|---|---|
| ' ' (space) | - $S$ is untested |
| 'i' | - the whole $S$ is independent |
| 'd' | - one of the proper subsets of $S$ is dependent |
| 's' | - $S$ is a simplex |

The procedure which modifies the vector- subset is called Procedure Modify.

Just after each modification *this* procedure always puts a space to the place of the info character (which is, for convenience, the last one of the string representing the set of vectors we investigate). The *main* program keeps testing whether the new vectorset is a simplex or not and fills out the last info character according to the test. After this the main program calls Procedure Modify for modifying the new vector-subset, and so on.

Clearly for each simplex the main program solves the system of linear equations 2.1 where the columns of the coefficient matrix are exactly the vectors of the actual simplex.

Now let us see Procedure Modify in more details, it is enclosed also at the end of the paper [$Sz$91].

$M$ denotes the number of all the given vectors, while $S$ will denote the set of the vectors *we just examine* (or shortly the indices of them only) with

the last information character, that is[1)]

$$S \subset \{1, 2, \ldots, M, \ ' \ ', \ 'i', \ 'd', \ 's'\} \quad .$$

Further, $\mathbf{c}$ always denotes an arbitrary character, $\mathbf{k}, \mathbf{t} \leq M$ and

$$\mathbf{T} \subseteq \{1, 2, \ldots, t-1\}$$

is any subset in the case $t$ is fixed. Now, the pseudocode of the main part of our algorithm is the following:

PROCEDURE MODIFY

**S** := {**1**};
**while not end do begin**
  **if** $S = \{k, k+1, \ldots, M; c\}$ **and** $c \neq d$ **then END;**
  **if** $S = \{k, k+1, \ldots, M; 'd'\}$ **then** $S := \{k, k+1, \ldots, M-1, M; \ ' \ '\}$;
  **if** $S = \{T, t, M; c\}$ **then** $S := \{T, t+1; \ ' \ '\}$;
  **if** $S = \{T, t; \ 'i'\}$ **then** $S := \{T, t, t+1; \ ' \ '\}$;
  **if** $S = \{T, t; \ 'd'\}$ **then** $S := \{T, t+1; \ ' \ '\}$;
  **if** $S = \{T, t; \ 's'\}$ **then** $S := \{T, t+1; \ ' \ '\}$;
**end ;**

The program does not miss any simplex because, roughly speaking, it checks the (candidate) subsets of the given vectorset in *lexicographical* order. Further, the program avoids repetition of output simplexes for the same purpose, for checking all possible candidates in *lexicographical* order.

A working routine in Pascal language is shown in the last Section of the present Chapter or in [*Sz*91].

### 3.1.1 The speed

One of the most crucial parts of the algorithm's speed is: how many times do we need to check the linear dependency of a subset $T \subseteq H$ of the input vectorset $H \subset \mathbb{R}^n$ for finding all the simplexes $S \subseteq H$ . For exact measurement of steps of algorithms the following notations are in use (see eg.[*CLR*]):

**Definition 3.1** *For any functions* $f, g : \mathbb{N} \to \mathbb{N}$ *we say that* $f = \mathcal{O}(g)$ *("**big oh of g**") iff for some positive constants* $c \in \mathbb{R}^+$ *we have*

$$\frac{f(n)}{g(n)} < c \quad ,$$

[1)] set theorists would call $S$ rather a sequence than a set

*that is*

$$f(n) < c \cdot g(n)$$

*for all* $n \in \mathbb{N}$ . $\square$

**Definition 3.2** *For any functions* $f, g : \mathbb{N} \to \mathbb{N}$ *we say that* $f = \Theta(g)$ (*"**big theta of g**") iff for some positive constants* $c_1, c_2 \in \mathbb{R}^+$ *we have*

$$c_1 < \frac{f(n)}{g(n)} < c_2 \quad ,$$

*that is*

$$c_1 \cdot g(n) < f(n) < c_2 \cdot g(n)$$

*for all* $n \in \mathbb{N}$ . $\square$

In some books we can find $\leq$ signs instead of $<$ in the above formulae, or the requirement "*for all* $n \geq n_0$ *for some fixed* $n \in \mathbb{N}$ " instead of for all "$n \in \mathbb{N}$ " as in our definitions above. These alteration does not effect significally the above Definitions, that is they are equivalent to the above ones, since the constants $c_i$ are all positive. (This equivalency can be seen easily.)

Further, as $[CLR, Section, 2.1.2]$ points out, some literature does not make any difference even between $\mathcal{O}$ and $\Theta$. Since in our Thesis we give upper bounds only to the speed of our algorithm, we use $\mathcal{O}$ only.

An easy analysis of the algorithm shows that our algorithm runs at most for $\mathcal{O}(M^{n+1})$ time (in the worst case) where $M = |H|$ is the size of the input. Since, all examined subsets of the $M$ vectors have size at most $n + 1$, the *spanned* dimension (=range) +1 of the input vectorset. This is *polynomial* time in $M$, the number of vectors. The results in Chapter 4 "*On the number of simplexes*" show that the maximal (possible) number of simplexes (=the size of the output) is really of this magnitude.

According to this estimation everyday size inputs (some dozen of vectors in 10–20 dimensional spaces) require some seconds only on modern computers. We used a Packard Bell IBM-compatible personal computer with 366 MHz CPU time, 16 MB RAM, Turbo Pascal 6.0 on DOS-shell of Windows 97. (We applied these simple computational tools succesfully for implementing and running our algorithm.)

Concrete computational experiments on (also large) datasets are shown in Chapter 8 "*Computational results*". The number of these checks is displayed in each of our examples in the last line of all the tables.

Perhaps a smart data-handling could avoid repeated checkings of subsets $T \subseteq H$ for their linear dependency, but we do not think it would fasten considerably our algorithm.

## 3.2 The extensions

Surprisingly enough a couple of related questions can also be solved by slight modifications *not* of the above algorithm *but* however of the input set of vectors only!

We explain here our ideas mainly refereeing for mechanisms, though the algorithm itself and the following ideas can be used in general in any other problem, in *any* linear space.

### 3.2.0 Reducing the dimension

Using some easy observations we can reduce the *size* of the input and so the running time of our computer.

**(a)** Clearly any vector (reaction) which is linearly independent of the others must be omitted since no simplexes could contain it. Though any systematic search for *all* these kind of vectors requires considerable time, for huge datasets (about 30 vectors in 30 dimension, i.e.hours of CPU time) this would offer a remarkable time saving, using some minute elementary algebraic computation.

For an outstanding example let us highligh here the case of Methane-Methanol example of $[HOS]$ (which is also our example 8.6 in Chapter 8) where especially the reactions $S_9$ and $S_{11}$ both contain exactly one extra species (a *single* co-ordinate), namely $C_2H_6$ and $CH_3OCH_3$ respectively, which do *not* occur in any other reactions. This clearly means that they must be linearly independent of the others. And in fact, $S_9$ and $S_{11}$ are not listed at all in Table X in $[HOS]$, which also can be seen in Chapter 8 : Table 8.6.a) shows the original example while in Table 8.6.b) we can see the effect of omitting $S_9$ and $S_{11}$ .

**(b)** If we have a vector with exactly *two* nonzero co-ordinates it may also be omitted and further the dimension of all the remaining vectors may be decreased by one.

In the language of *chemistry*: such a vector stands for a reaction of type

$$A = \lambda B$$

for some (positive) number $\lambda \in \mathbb{R}$. This clearly implies that the species (groups of atoms/ functional bonds) $A$ and $B$ are equivalent. That is, the species $A$ can be replaced to $\lambda B$, for example, in all the other reactions while the species $A$ and the reaction $A = \lambda B$ can be omitted. (Eg. $C_6H_6 = 3C_2H_2$ .) This decreases both the number of species (dimension) and of reactions (vectors). Of course to each mechanism $\mathcal{M}^-$ in this reduced lower dimensional space we might add the reaction $A = \lambda B$ if the species $B$ occurs in $\mathcal{M}^-$ to form a real mechanism $\mathcal{M}$ in the original problem. (Of course $\mathcal{M}$ must *not* be minimal, so if we search for *minimal* mechanisms we might have also to examine its minimality after.)

Let us examine this construction in the language of *mathematics*, too.

**Construction.** Let the vectorset $H \subseteq \mathbb{R}^N$ be given and suppose that the vector $\mathbf{X} \in H$ has *exactly two* nonzero co-ordinates $x_u = \lambda \cdot x_v$ where $\lambda \in \mathbb{R}\backslash\{0\}$ is arbitrary nonzero real number and $\mathbf{X} = [x_1, \dots, x_N]^T$. For each vector $\mathbf{Y} \in H$ let us now substract the v'th co-ordinate $\lambda$-times from the u'th one and delete the v'th co-ordinate from $\mathbf{Y}$ to get the vector $\mathbf{Y}^- \in \mathbb{R}^{N-1}$.

In formula: from the vector $\mathbf{Y} = [y_1, \dots, y_N]^T \in \mathbb{R}^N$ we construct the vector

$$\mathbf{Y}^- := [y_1, \dots, y_u - \lambda \cdot y_v, \ \dots, y_{v-1}, y_{v+1}, \ \dots, y_N]^T \quad \in \mathbb{R}^{N-1}$$

if we suppose $u < v$ . $\square$

Clearly $\mathbf{X}^- = \mathbf{0}$ .

Let now

$$H^- := \{\mathbf{Y}^- \mid \mathbf{Y} \in H, \ \mathbf{Y} \neq \mathbf{X}\} \subseteq \mathbb{R}^{N-1} \quad .$$

**Lemma 3.3** *For any* $S^- \subseteq H^-$ *we have that* $S^-$ *is linearly independent iff the set* $S \cup \{\mathbf{X}\}$ *is linearly independent, where* $S := \{\mathbf{Y} \mid \mathbf{Y}^- \in S^-\}$ .

**Proof.** Let $S := \{\mathbf{Y}_i | i \leq t\}$ . Since only the u'th co-ordinates of the vectors $\mathbf{Y} \in H$ were changed, and further all other co-ordinates of $\mathbf{X}$ were $\mathbf{0}$ which were not deleted, we have to focus on the u'th co-ordinates $y_u^i$ of $\mathbf{Y}_i$ only. (Recall that the u'th co-ordinate of $Y_i^-$ is $y_u^i - \lambda \cdot y_v^i$ .) This means,

that for any set of coefficients $\mu_1, \ldots, \mu_t \in \mathbb{R}$ we have

$$\sum_{i=1}^{t} \mu_i \mathbf{Y}_i^- = \mathbf{0} \quad \textit{iff} \quad \sum_{i=1}^{t} \mu_i (y_u^i - \lambda \cdot y_v^i) = 0$$

$$\textit{iff} \quad \sum_{i=1}^{t} \mu_i y_u^i = \lambda \cdot \sum_{i=1}^{t} \mu_i y_v^i =: c$$

$$\textit{iff} \quad \sum_{i=1}^{t} \mu_i \mathbf{Y}_i = \frac{c}{x_u} \cdot \mathbf{X} \quad .$$

■

Now let us consider any subset $S^- \subseteq H^-$ . Using the previous lemma we have that $S^-$ is simplex *iff* $S \cup \{\mathbf{X}\}$ is dependent and $S \backslash \{\mathbf{Y}\} \cup \{\mathbf{X}\}$ is independent for all $\mathbf{Y} \in S$ , $\mathbf{Y} \neq \mathbf{X}$ *iff* either $S \cup \{\mathbf{X}\}$ is a simplex or $S$ is dependent but in the latter case we must have a simplex $T \subseteq S$ not containing $\mathbf{X}$ . Using this observation we can reduce the search for simplexes in $H$ : we have to search for them among the set $S \cup \{\mathbf{X}\}$ and all the subsets of $S$ for every simplex $S^- \subseteq H^-$ .

Let us emphasize that we did not mention such difficulties above when we spoke in the language of chemistry. There we did not bother of finding *minimal original reactions* in the previous paragraph what caused this difference.

This reduction is illustrated in our example 8.7 "*Glucose to Pyruvate Conversion*" in Chapter 8 which is taken from [*HOS*90].

In this example the original problem proposed 14 vectors in the 13 - dimensional space, but introducing 3 new technical vectors we finally started with 17 vectors. (The role and use of these technical vectors is explained in Subection 3.2.1.i.) The first part of Table 8.7 shows this original problem which required 93 seconds on our computer.

However, applying the above reduction for all the *eight* reaction of type $A = \lambda B$ , we reached to a problem containing only 9 vectors in the 6-dimensional space. This input required 0.10 seconds, details are shown in the middle part of Table 8.7.

For the last part we applied one *further reduction* for a resulted new reaction of this type. The CPU time decreased from 93.00 to 0.00 seconds! (Of course, by 0.00 sec we mean that we measured the CPU time with precisity 0.01 seconds and the last run required less than 0.01 seconds.) We have to admit, that we did not make any computations for decoding – finding simplexes in the original problem from the reduced ones, so far.

### 3.2.1 Searching for (direct) overall reactions

In this subsection we consider the case when the resulting (overall) reaction

$$\mathbf{X}_{k+1} = \mathcal{R}(\underline{\lambda})$$

is *not* known but the lists of the *terminal (chemical) species* (what we want to synthese and what are the initial ones), and *intermediate (active) species* (which occur only during the mechanism) are given. (For terminology see [$HS83$] or our Section 2.2 in Chapter 2 above). Remark that all species are supposed to be either terminal or intermediate ones.

Our goal now is to find *all* mechanisms of which corresponding reactions contain terminals (chemical) species only, these reactions are called **overall** ones. Again, our algorithm provides minimal mechanisms (i.e.**direct** or **cycle-free** ones) with their minimal (i.e.simple) reactions.

**(i)** For this purpose enlarge first the given set of vectors $\{\mathbf{X}_1, ..., \mathbf{X}_k\} \subseteq \mathbb{R}^N$ with new "ideal" vectors $\mathbf{V}_t \in \mathbb{R}^N$ to separate terminate and intermediate species: one new vector $V_t$ for each terminate species $A_t$ where $t \in T$. In more detail, let all but the $t$ -th co-ordinates of $V_t$ be equal to 0 while let the $t$ -th co-ordinate (representing $A_t$) of $V_t$ be equal to 1.

Now, from *any* mechanism

$$\sum_{j=1}^{k} \lambda_j \cdot X_j + \sum_{t \in T} \mu_t \cdot V_t = \mathbf{0} \tag{3.1}$$

we can extract the overall reaction

$$R := -\sum_{t \in T} \mu_t \cdot V_t \tag{3.2}$$

where, as usual, the initial species are with negative coefficients and the synthesed ones with positive coefficients. Clearly now the mechanism

$$\mathcal{M} := \sum_{j=1}^{k} \lambda_j \cdot X_j \tag{3.3}$$

has exactly the resulting (overall) reaction

$$\mathcal{R}(\mathcal{M}) = \mathbf{R} \, .$$

Of course we have to consider only the simplexes of the extended vectorset

$$S \subseteq \{\mathbf{X}_1, ..., \mathbf{X}_k\} \cup \{V_t \mid t \in T\} \tag{3.4}$$

which contain at least one new vector $V_t$ . Otherwise we would get mechanisms $\mathcal{M}$ resulting the void reaction $\mathcal{R}(\mathcal{M}) = \mathbf{0}$ (as without introducing the new vectors $\{V_t \mid t \in T\}$) .

We have to find *simplexes* $S$ in the set (3.4) since we are interested in *minimal* mechanisms. This might be an essential restriction for finding *all* mechanisms. In (iii) below we discuss another, two-stage solution for finding *all* minimal (direct) overall reactions and minimal mechanisms resulting the corresponding overall reaction, though the method we just presented is a direct, *one-stage* one for the same problem. In Section 3.3 we give an exact mathematical proof for that the present method and the one in (iii) give the *same* output. In other words, the above method based on (3.3) and (3.4) really gives *all* minimal reactions and their minimal mechanisms. So we can use our algorithm automatically in *one stage* as we discussed above in (3.3) and (3.4), which means a fast solution to our problem.

After we have extended our vectorset $\{\mathbf{X}_i : i \leq k\}$ with the new vectors $\{\mathbf{V}_j : j \in T\}$ to the set

$$H := \{\mathbf{X}_i : i \leq k\} \cup \{\mathbf{V}_j : j \in T\}$$

we may run our algorithm either for finding

$$\textit{all} \text{ simplexes in } \quad H \tag{\textbf{VarAll}}$$

or *only* those which contain at least one of the *new* vectors

$$\textit{only} \text{ intersecting } \quad \{\mathbf{V}_j : j \in T\} \tag{\textbf{VarOnly}}$$

and we can compare these runs to when we searched for all simplexes in the *original* vectorset

$$\text{in the original } \quad \{\mathbf{X}_i : i \leq k\} \quad . \tag{\textbf{VarOrig}}$$

Clearly for all computational quantities $\nu$ (for eg. time, number of simplexes, checked subsets,etc.) we must have

$$\nu(VarAll) = \nu(VarOnly) + \nu(VarOrig). \tag{3.5}$$

This easy fact can be also seen in each of in Tables 8.5 through 8.7 in Chapter 8 "*Computational results*".

**(ii)** We must not forget about the *law of mass balance (preservation of the material)* in the mechanism $\mathcal{M}$ which results the reaction

$$\mathbf{R} = \mathcal{R}(\mathcal{M}) = -\Sigma_{t\in T}\mu_t \cdot V_t$$

by (3.2).

This is not a problem from *chemical* point of view: since all the given reactions (input vectors) satisfy this law, their linear combination satisfies, too, since by (3.1) we have $\mathbf{R} = \Sigma_{j=1}^{k}\lambda_j \cdot X_j$ . (In other words, this law holds automatically for the output mechanism assuming it hold for all of the input reactions.)

From *mathematical* point of view: this law is equivalent to that the vector $\mathbf{R} \in \mathbb{R}^N$ must satisfy the requirement

$$\mathbf{B} \cdot \mathbf{R} = \mathbf{0} \tag{3.6}$$

for the matrix $\mathbf{B} \in \mathbb{R}^{m\times N}$ which codes the sum-formulae of *all* the species (groups of atoms/ functional bonds) involved in our problems: in any of the input vectors $\{\mathbf{X}_i : i \leq k\}$ did it, as we described in Chapter 2.

The equality (3.6) might be curious if we used only (3.2) as $\mathbf{R} = -\Sigma_{t\in T}\mu_t \cdot V_t$ , but using

$$\mathbf{R} = \sum_{j=1}^{k} \lambda_j \cdot X_j \tag{3.7}$$

from (3.1) and the assumption

$$\mathbf{B} \cdot X_j = \mathbf{0} \qquad (\forall j \leq k)$$

we clearly have

$$\mathbf{B} \cdot \mathbf{R} = \sum_{j=1}^{k} \lambda_j \mathbf{B} X_j = \mathbf{0} \quad .$$

For an additional explanation of the proof in Section 3.3 below, let us mention the next variant for ensuring the law of the mass balance. Let us first enlarge the dimension of all the vectors $\{\mathbf{X}_i : i \leq k\}$ and $\{V_j : j \leq t\}$ with as many new co-ordinates as many atoms the vectors $\{V_j : j \in T\}$ (i.e.

the *terminate* species) are built up. Next, let us code the sum-formula of these new vectors $V_j$ in their own new co-ordinates as we described in Chapter 2, while we let all the new co-ordinates of the old vectors $\{\mathbf{X}_1, ..., \mathbf{X}_k\}$ to be equal to 0. We do *not* think it would be interesting to present such computational runs which, of course, would gave the same results but in some more time!

Let us emphasize again that running our algorithm with the modified dataset (as in (i)) we immediately get (in one run) *also* the steady-state *mechanism*

$$\mathcal{M} := \sum_{j=1}^{k} \lambda_j \cdot X_j$$

with $\mathcal{R}(\mathcal{M}) = R$ , that is the mechanisms which yield exactly the given reaction $R$. Since our algorithm lists *all* simplexes of the vectorset

$$\{\mathbf{X}_i : i \leq k\} \cup \{\mathbf{V}_j : j \in T\}$$

in its full run, we have only to separate all mechanisms corresponding to several reactions, so we get *all* (direct) steady-state mechanisms with *all* their (simple) overall reactions in a single run. This means that in the present case there is *no* need for further running the variant described in subsection 3.2.2.

**(iii)** *Another variant* to the problem of finding all minimal overall reactions and minimal (direct) mechanisms leading to them would be the following.

Let us first search *all* the possible minimal reactions among the terminate species as it is described in Chapter 2. Then, for each minimal reaction let us search separately the minimal (direct/steady state) mechanisms among the original given set of reactions, which mechanisms belong to the actual minimal reaction as described in the next Subsection 3.2.2.

This idea requies *several* lower dimensional runs of our algorithm (and transfering data among them) instead of a single higher dimensional one as we suggested in (i). Let us warn however our Readers that in the preliminary search for all the possible minimal reactions among the terminate species we may get also reactions which can *not* be built up from the original given set of reactions and so imply void runs in the next step !

Computational examples for these comparisons are presented in the examples 8.5 through 8.7 in Chapter 8.

Example 8.5 and Table 8.5 are the most illustrative. In the original problem we were given 7 vectors $S_i$ in dimension 10 and 4 terminal species built up from 3 element.

The first column "*Terminal species*" of Table 8.5 shows the preliminary run of our algorithm listing all the possible reactions $d_1, ..., d_4$ among the 4 terminate species (mentioned in (i) above). In the other steps we did not any use of this computation for the other columns[(2)].

Column 2 of Table 8.5 shows the search for all possible mechanisms among the original reactions, or, in other words, linear combinations (i.e. simplexes) of the given vectors $S_i$ resulting the zero vector, i.e. the void reaction. The single mechanisms we found shows that the reactions $S_1, \ldots, S_7$ are *not* linearly independent.

Columns 3 and 4 show computation when we introduced the new vectors $V_1, \ldots, V_5$ representing one-to-one the terminal (chemical) species as we suggested in the first part of Section 3.2. For comparison of CPU time we run the algorithm first for *all* simplexes then for those which contain at least one new vector $V_i$ only. That is, both without and with halting the programme after leaving all new vectors, Column 3 and 4 show the differences. Our algorithm found the total 12 minimal mechanisms $m_j$ in 1.87 seconds.

### 3.2.2 (Direct) steady state mechanisms

In this subsection we deal with the case when we *do* know already one or more resulting (overall) reactions (determined either by chemical or other mathematical method) to which we want to determine all the (minimal) mechanisms leading to these given reactions.

Let us deal first with the case when we are given a single resulting reaction $R$. For our purpose let us first extend the given vectorset

$$H := \{\mathbf{X}_1, ..., \mathbf{X}_k\}$$

with the new vector $\mathbf{X}_{k+1} := R$ and then let make our algorithm list *only* the simplexes containing $R$ .

Since any mechanism (3.7) which results the reaction $R$ can be trivially transformed to the vanishing linear combination

$$\sum_{j=1}^{k+1} \lambda_j \cdot X_j = \mathbf{0}$$

[2)] So far we did not made any computer experiments for the idea presented in (iii) since all our computations concerning mechanisms were below 25 minutes, the long-running example in Section 8.4 is for all the minimal mechanism where the resulting (overall) reaction is already given.

(which is called a *cycle* in [S84]), we should only substract $\mathbf{X}_{k+1}$ from the above equality and the remaining mechanism

$$\mathcal{M} := \frac{-1}{\lambda_{k+1}} \sum_{j=1}^{k} \lambda_j \cdot X_j$$

would certainly result the reaction $R$ , that is $\mathcal{R}(\mathcal{M}) = R$ . $\mathcal{M}$ is minimal of course.

Since we are looking only for simplexes which do contain the fixed vector $R = \mathbf{X}_{k+1}$ , we have to apply our bounding formulas from Chapter 4 "*On the number of simplexes*" for $k$ many vectors only! In other words, the computing time decreases by a factor of approximately

$$\frac{k-n}{k+1} = 1 - \frac{n+1}{k+1}$$

when we search for simplexes containing $\mathbf{R}$ (as a fixed element) instead of containing all possible subsets of $H \cup \{R\}$ , which is a $(k+1)$ -element subset of $\mathbb{R}^n$.

The above trick can be extended easily to the case when we are given more than one fixed resulting (overall) reactions $\mathbf{R}_1, \ldots, \mathbf{R}_t$ at the same time. We simply have to add these vectors to $H$ and we have to consider only the simplexes

$$S \quad \subseteq \quad H \cup \{\mathbf{R}_1, \ldots, \mathbf{R}_t\}$$

which contain *exactly one* of the new vectors $\mathbf{R}_1, \ldots, \mathbf{R}_t$ . Clearly this parallel computing is adviced for small $t$ only since we are interested in simplexes $S$ with this property and checking that

$$|S \cap \{\mathbf{R}_1, \ldots, \mathbf{R}_t\}| = 1$$

would require some time for large $t$. For large $t$, which has magnitude of $k$, we recommend to run this modified algorithm separately for each set $H \cup \{\mathbf{R}_i\}$ for all $i \leq t$ .

### 3.2.3 Neither reactions nor terminate species are known

We can also handle the case when *no* terminal (chemical) species are selected at all at the beginning but we want to find all overall reactions. By our algorithm we search for all the possible simplexes and compute (all) the corresponding resulting (overall) reactions which give the answer. Observe however that in the meantime we have already listed the corresponding overall mechanisms, too. This means that there is no need for any further computing.

## 3.3 Proof of the equivalence

In this Section we give a (mathematical) proof for the equivalence of the variations of our algorithm given in (i) and in (iii) in Subsection 3.2.1. Namely, we justify that the same set of *all* direct overall reactions and their minimal mechanisms can be obtained either with the one-stage method described in (i) or the two-stage variant introduced in (iii) in Subsection 3.2.1.

So, we are given the (arbitrary) vectorset

$$\{\mathbf{X}_1, \ldots, \mathbf{X}_k\} \subseteq \mathbb{R}^n$$

Let further

$$\{\mathbf{V}_1, \ldots, \mathbf{V}_t\} \subseteq \mathbb{R}^n$$

be *any* set of linearly independent set of vectors where $t \leqq n$ . Let us denote the set of all these vectors by $H$ , i.e. let

$$H := \{\mathbf{X}_j : j \leq k\} \cup \{\mathbf{V}_i : i \leq t\} \quad .$$

We have to prove the equivalence of the simplexes of the vectorset $H$ and those of $\{\mathbf{X}_j : j \leq k\} \cup \{\mathbf{S}_R\}$ for *certain* vector $\mathbf{S}_R \in \mathbb{R}^n$.

**Theorem 3.4** *For any simplex* $S \subseteq H$ , $S = \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{V}_i : i \in T\}$ *where* $K \subseteq \{1, \ldots, k\}$ *and* $T \subseteq \{1, \ldots, t\}$ *are nonempty subsets, and for the vector*

$$\mathbf{S}_R := -\sum_{j \in K} \mu_j \cdot \mathbf{X}_j = \sum_{i \in T} \lambda_i \cdot \mathbf{V}_i \tag{3.8}$$

*(for the suitable coefficients* $\mu_j, \lambda_i \in \mathbb{R}$*), the set*

$$S' := \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{S}_R\}$$

*is also a simplex.*

**Proof.** Since $S$ is minimal dependent, all the coefficients in (3.8) must be different from 0. Then Lemma 2.5 completes the proof. ■

The above Theorem ensures that the method we described in (i) of Subsection 3.2.1 finds all simplexes (solutions) what the other variation in (iii) has found.

We will prove the other direction in Theorem 3.5 below, what is not true for any set $H$ of vectors and simplex $S' = \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{S}_R\}$ , we also need the additional assumptions (*First*) through (*Fifth*) below.

**First**, we need that all the vectors $\mathbf{X}_j \ \ (j \leq k)$ satisfy

$$\mathbf{B} \cdot \mathbf{X}_j = \mathbf{0} \qquad (\forall j \leq k) \tag{3.9}$$

for a given (arbitrary) matrix[3] $\mathbf{B} \in \mathbb{R}^{m \times n}$ , though this is not required for the vectors $\mathbf{V}_i \ \ (i \leq t)$ ! Denote now

$$\{b_i : i \leq n\} \subseteq \mathbb{R}^m$$

the set of column - vectors of $\mathbf{B}$ .

**Second**, we need that the vectors $\mathbf{V}_i \ \ (i \leq t)$ are the first $t$ standard base vectors of $\mathbb{R}^n$, that is all but the i'th co-ordinates of $V_i$ are equal to 0 while the i'th co-ordinate equals to 1.

**Third**, we have to observe the connection

$$\mathbf{B} \cdot \mathbf{V}_i = \mathbf{b}_i \quad (\forall i \leq t)$$

(which is a trivial consequence of Second).

Recall now that we want to prove that each solution (minimal overall reaction and direct mechanisms) received from the variant (iii) of our algorithm (in Subsection 3.2.1) will also be provided by the variant in (i) ibid. This implies the following assumptions we may use:

**Fourth**, let the vector $\mathbf{S}_R$ in (3.8) and let the set

$$S' = \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{S}_R\}$$

be a simplex. By (iii) of Subsection 3.2.1 we also have that the set

$$\{\mathbf{b}_i : i \in T\} \subseteq \mathbb{R}^m$$

is also a simplex!

Let us mention that by (3.8) we have

$$\mathbf{0} = \mathbf{B} \cdot \sum_{j \in K} \mu_j \mathbf{X}_j = \sum_{i \in T} \lambda_i \mathbf{B} \cdot \mathbf{V}_i = \sum_{i \in T} \lambda_i \mathbf{b}_i \tag{3.10}$$

[3] For chemists: $\mathbf{B}$ codes the sum-formulae of *all* the species involved in the input reactions $\mathbf{X}_j \ \ (j \leq k)$ as we described in Section 2.1.

which implies that $\{\mathbf{b}_i : i \in T\}$ is dependent for *any* vector $\mathbf{S}_R$ satisfying (3.8).

The above result (Fourth) implies the below one which will be useful in our proof:

**Fifth,** the above set of indices $T$ satisfies the following minimality property:

*" $T \subseteq \{1, \ldots, t\}$ is minimal in the sense that there is no proper subset $T' \subsetneqq T$ for which*

$$\sum_{j \in L} \mu'_j \mathbf{X}_j = \sum_{i \in T} \lambda'_i \mathbf{V}_i \tag{3.11}$$

*would hold for some $L \subseteq \{1, \ldots, k\}$ . "*

Now we are ready to prove the converse of Theorem 3.4.

**Theorem 3.5** *Let*

$$S' = \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{S}_R\} \subseteq \mathbb{R}^N$$

*be any simplex where $\mathbf{S}_R$ satisfies (3.8), further the above assumptions (First) through (Fifth) hold.*

*Then the set*

$$S := \{\mathbf{X}_j : j \in K\} \cup \{\mathbf{V}_i : i \in T\}$$

*is also a simplex.*

**Proof.** $S$ is clearly dependent by (3.8). The sets $S \backslash \{\mathbf{V}_{io}\}$ for each $i_0 \in T$ are independent using the minimality property (3.11) for $T$ since (Fourth) implies that $T$ is nonempty.

Let now $j_0 \in K$ be arbitrary and suppose by contradiction that the set $S \backslash \{\mathbf{X}_{jo}\}$ is dependent. Let further

$$\mathbf{S}_Q := -\sum_{j \in K} \mu'_j \mathbf{X}_j = \sum_{i \in T} \lambda'_i \mathbf{V}_i \tag{3.12}$$

for some $\mu'_j, \lambda'_i \in \mathbb{R}$ where $\mu'_{j_0} = 0$ . Arguing now as in (3.10) we get

$$\mathbf{0} = -\mathbf{B} \cdot \sum_{j \in K} \mu'_j \mathbf{X}_j = \sum_{i \in T} \lambda'_i \mathbf{B} \cdot \mathbf{V}_i = \sum_{i \in T} \lambda'_i \mathbf{b}_i \quad . \tag{3.13}$$

Since the set $\{b_i : i \in T\}$ is simplex, all solutions of the homogeneous equality

$$\mathbf{0} = \sum_{i \in T} \gamma_i \mathbf{b}_i$$

are parallel, this is an another easy characterization of simplexes. For our equalities in (3.10) and in (3.13) this implies that the coefficient vectors $[\lambda_i : i \in T]^T$ and $[\lambda' : i \in T]^T$ are parallel. This would imply by (3.8) and (3.12) that the vectors $S_Q$ and $S_R$ were also parallel, i.e. $S_Q = \tau \cdot S_R$ would hold for some $\tau \in \mathbb{R}$ . Using (3.8) and (3.12) again this leads to a contradiction since the vectors $\{\mathbf{X}_j : j \in K\}$ were supposed to be independent, moreover $\mu'_{j_0} = 0$ but also *none* of the coefficients $\mu_j$ was 0 , finally $S_Q$ may not be the zero vector. ■

The above Theorem clearly justifies that each solution (minimal overall reaction and direct mechanisms) produced by the variant (iii) of Subsection 3.2.1 is also be given by the other one in (i) of the same subsection.

## 3.4 Comparison to other algorithms

In this Section we compare the problems what other algorithms in the literature solve and their speed only. As we pointed out, all these and our methods give the *same* outputs for the same inputs.

The first algorithm for generating reaction mechanisms I met was **J.Happel-P.H.Sellers- M.Otarod** 's one, published in [$HOS90$] which mainly used elementary matrix operations and linear combinations of linear equations. Their method is rather theoretical with some manual computations. It uses elementary matrix operations for reducing the system of linear equations, and uses heuristic find for bases of the set of all solutions. In their paper the authors do not give all details of the algorithm, which searches reaction mechanisms only and not simplexes in general. As the authors announce in their paper, a computer program in Fortran language is available. This program, with the small examples supported runs for seconds only, we did not tried it with larger examples.

Recently **B.Bertók** evaluated an algorithm, based on graph theoretic concepts, using some linear programing. His algorithm is explained in his Thesis [$B99$] and his joint paper [$FBF00$] with **L.T.Fan** and **F.Friedler**. He considers not only the species contained in the given reactions but displays the connections among these reactions in a bipartite directed graph, usually called a P-graph or PNS -network. In a P-graph we have two types of vertices:

one for reactions and the other for species. We connect each reaction with its input and output species with directed edges, in Figure 7.1 we can see a typical P-graph. Minimal reactions mean circle-free paths from the starting to the final terminal species in P-graphs. Bertók searches for these circle-free paths with linear algebraic and graph-theoretical tools with the help of Linear Programing. The author of the present Thesis had the opportunity to compare both the outputs and the speed of his and Bertók's algorithm (most of these test examples are listed in Chapter 8). As we mentioned, the outputs are the same, running times are of the same magnitude.

If we search only for the *set* of the reactions taking part in a minimal (circle-free) mechanisms, without any interest on the *order* of these reactions, our linear algebraic model is sufficient. Positive and negative entries of any vector distinguish in- and out- species of the corresponding reaction, no further directed graph is neccessary for *this* purpose.

In the paper of **S.Kumar** and **Á.Pethő** [$KP85$] and also in [$CMW90$] of **C.Chevalier**, **H.Melenk** and **J.Warnatz** the authors talk about *one* computing examples but we could not find details of any algorithm. They also do not give details of larger size examples nor their computing experiments. So we could not compare their algorithm to ours.

The output lists all of these algoritms (of course) are either identical or can be converted easily to each other. As to our information the other algorithms do *not* use less time than our algorithm above. We think that running small test-examples on modern personal computers can not reveal the difference of the speeds of the different algorithms.

More details are supplied in Chapter 8.

## 3.5 A program list

We do not include the whole source code of our program since only the modifying procedure is of interest. However let us include this procedure here in full detail, being it is very short.

```
meretx := M ;            { the number of input vectors }
PROCEDURE MODIFY;        { modifying the vector - list }
var hossz,elso,utolso : integer ;
label ret ;
begin
 hossz := length(szimplex) ;
```

```
elso := ord(szimplex[1]) - 64 ;
utolso := ord(szimplex[hossz-1]) - 64 ;
if szimplex[hossz]=' ' then goto ret ;       { not checked }
if (elso+hossz-2=utolso) and (utolso=meretx) and ('d'<>szimplex[hossz])
   then begin       { end sequence }
   vege := true ;       { program ends }
   goto ret ;
   end ;
if (elso+hossz-2=utolso) and (utolso=meretx) and ('d'=szimplex[hossz])
   then begin       { end sequence }
   utolso := ord(szimplex[hossz-2]) + 1 ;       { new last item }
   sstr := copy(szimplex,1,hossz-3) + char(utolso) + ' ' ;
   szimplex := sstr ;
   goto ret ;
   end ;
if utolso=meretx then       { end reached but }
   begin         { not end sequence }
   utolso := ord(szimplex[hossz-2]) + 1 ;       { new last item }
   sstr := copy(szimplex,1,hossz-3) ;
   szimplex := sstr + chr(utolso) + ' ' ;
   goto ret ;
   end ;
if szimplex[hossz]='i' then       { independent => enlarging }
   begin
   szimplex[hossz] := chr(utolso+64+1) ;
   szimplex := szimplex + ' ' ;
   goto ret ;
   end ;
if szimplex[hossz]='d' then       { dependent => new last item }
   begin
   szimplex[hossz-1] := char(ord(szimplex[hossz-1])+1) ;
   szimplex[hossz] := ' ' ;
   goto ret ;
   end ;
if szimplex[hossz]='s' then       { simplex => test another }
   begin
   szimplex[hossz-1] := char(ord(szimplex[hossz-1])+1); {last enlarging}
   goto ret ;
   end ;
ret : ;
end ;       { proc.modify }
```

# Chapter 4

# On the number of simplexes

The main question of the present Chapter is:

*How many simplexes (minimum or maximum) can be found in a given set of vectors* $\mathcal{H} \subset \mathbb{R}^n$ **and** *what are the extreme configurations, if only the dimension of the space* $(n)$ *and the size of the vectorset* $\mathcal{H}$ *is fixed ?*

In other words, we want bounds for simplexes (minimal reactions) whenever the dimension (number of possible atoms) and the size of the given vectorset (number of species) are given. (Recall, that a set of vectors $\mathcal{S} \subset \mathbb{R}^n$ is called a *simplex* iff $\mathcal{S}$ itself is linearly dependent but all its subsets are independent.)

Let us observe that we have to assume that $\mathcal{H}$ spans $\mathbb{R}^n$ , or in other words, $n$ is the dimension of the spanned subspace $[\mathcal{H}]$ of $\mathcal{H}$ , since, our formulae on the number of simplexes must contain also the quantity $n$ .

As we indicated in the introduction, to determine the *extreme configurations* is the real problem, the *number* of the simplexes is just a corollary.

For this purpose we introduce the following notations.

**Definition 4.1** ***(i)*** $\mathbf{simp}(\mathcal{H})$ *denotes the number of simplexes contained in* $\mathcal{H}$ *for any set of vectors* $\mathcal{H} \subset \mathbb{R}^n$.

***(ii)*** *For any set of vectors* $\mathcal{S} \subset \mathbb{R}^n$ *we denote by* $[\mathcal{S}]$ *the* ***spanned subspace*** *(in other words, the linear hull, or the algebraic closure ) of* $\mathcal{S}$.

***(iii)*** *A simplex is called* ***small*** *if it contains just two elements (parallel ones), otherwise it is called* ***large.*** *A* $k$***-simplex*** *denotes a simplex of size* $k$ . □

Now, our main results in the present chapter are the following:

**Theorem** (see Thm.4.3) *For any $\mathcal{H} \subset \mathbb{R}^n$ of fixed size (so that $\mathcal{H}$ spans $\mathbb{R}^n$), $simp(\mathcal{H})$ is* maximal *if and only if any $n$ vectors of $\mathcal{H}$ are linearly independent.* □

**Theorem** (see Thm.4.5) *For any $\mathcal{H} \subseteq \mathbb{R}^n$ of fixed size (so that $\mathcal{H}$ spans $\mathbb{R}^n$), $simp(\mathcal{H})$ is* minimal *if and only if $\mathcal{H}$ consists of $n$ linearly independent equivalence classes of sizes differing by at most one from each other, where each equivalence class is a set of parallel vectors.* □

**Corollary** (see Cor.4.10) *Let $\mathcal{H} \subseteq \mathbb{R}^n$ so that $\mathcal{H}$ spans $\mathbb{R}^n$ and $|\mathcal{H}| = m$. Then, writing $m = an + b$ where $0 \leq b < n$ , we have*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(\mathcal{H}) \leq \binom{m}{n+1} \quad .$$

*and the extreme values may be achieved only in the unique configurations described in the above theorems.*

*Especially, when $m$ is divisible by $n$ (i.e. $b = 0$), then we have*

$$n \cdot \binom{\frac{m}{n}}{2} \leq simp(\mathcal{H}) \leq \binom{m}{n+1} \quad . \qquad \square$$

The question for the minimum value of $simp(\mathcal{H})$ is *open* if no parallel vectors are allowed in $\mathcal{H}$. Unfortunately our methods in the minimum case work only if we allow parallel vectors (ie. to use the same species more than one time). So the lower bound must be much larger when excluding parallel vectors, but at this time the question for the minimum value of $simp(\mathcal{H})$ is open if no parallel vectors are allowed in $\mathcal{H}$ . (This restriction is irrelevant in the maximum case.)

The special case $n = 3$ when excluding parallel vectors is dealt in Section 4.3 in the next Theorem:

**Theorem** (see Thm.4.11) *For any $\mathcal{H} \subseteq \mathbb{R}^3$ of fixed size not equal to 3, 4 or 7 such that $\mathcal{H}$ spans $\mathbb{R}^3$ and contains* **no** *collinear vectors, $simp(\mathcal{H})$ is minimal if and only if $\mathcal{H}$ is contained in two intersecting planes, one of which is of size 3; i.e. precisely when $\mathcal{H}$ contains three linearly independent vectors $\{u_1, u_2, u_3\}$, another vector $v$ coplanar with $u_1$ and $u_2$ and the rest $\mathcal{H} \backslash \{u_1, u_2, u_3, v\}$ coplanar with $u_2$ and $u_3$ .* □

For $|\mathcal{H}| = 3$, $\mathcal{H}$ must consist of 3 linearly independent vectors as it is required to span $\mathbb{R}^3$, and therefore $simp(\mathcal{H}) = 0$ . For $|\mathcal{H}| = 4$, there are 2 optimal configurations with 1 simplex. The optimal configurations are explained below in Figures 1 and 2 in the third Section.

Higher dimensions are discussed in Chapter 7 "*Beyond this thesis*".

## 4.1 The maximum case

The question of *maximal* number of simplexes *and* finding the (unique) extreme configuration, in a given set of vectors $H \subset \mathbb{R}^n$, is relatively easy and requires no special assumption (as in the case of minimal number of simplexes) on the set of given vectors.

Let us emphasize that if we asked only the maximal *number* of simplexes, Sperner's wellknown theorem in combinatorics (see eg. $[Sz01n]$ or below) would serve us an easy solution for the maximal *number* of simplexes:

**Theorem 4.2** ***(Sperner, 1930)*** *For any set $S$ of size $m$ , $k \leq \frac{m}{2}$ and subsets $A_1, ..., A_\ell \subsetneqq S$ such that $|A_i| \leq k$ and*

$$A_i \not\subseteq A_j \qquad \text{for } i, j \leq \ell,\ i \neq j \tag{4.1}$$

*we must have $\ell \leq \binom{m}{k}$ .* $\square$

The assumption (4.1), which is called **Sperner-property**, clearly holds if $A_i$ is simplex for each $i \leq \ell$ .

However, in our theorems below we explore also the *structure* of the maximal configurations, i.e. *which* subsets $\mathcal{H} \subset \mathbb{R}^n$ may contain the *maximal* possible number of simplexes.

**Theorem 4.3** *For any $\mathcal{H} \subset \mathbb{R}^n$ of fixed size (so that $\mathcal{H}$ spans $\mathbb{R}^n$), $simp(\mathcal{H})$ is maximal if and only if any $n$ vectors of $\mathcal{H}$ are linearly independent.*

**Proof.** Fix $\mathcal{H} \subset \mathbb{R}^n$ of size $m$. Choose $\mathcal{V} = \{v_1, v_2, ..., v_n\} \subseteq \mathcal{H}$ spanning $\mathbb{R}^n$, and suppose $u \in \mathcal{H} \backslash \mathcal{V}$ belongs to a linearly dependent subset of $\mathcal{H}$ of size at most $n$. Choose $u' \in \mathbb{R}^n$ not in any subspace generated by any $n-1$ elements of $\mathcal{H}$. Define now

$$\mathcal{H}' := (\mathcal{H} \backslash \{u\}) \cup \{u'\} .$$

Then $|\mathcal{H}'| = |\mathcal{H}|$ and we first show that $simp(\mathcal{H}') \geq simp(\mathcal{H})$ .

So let $\mathcal{S} = \{u_1, u_2, ..., u_k\} \subseteq \mathcal{H}$ be a simplex of $\mathcal{H}$. If $u \notin \mathcal{S}$ then $\mathcal{S}$ is still a simplex of $\mathcal{H}'$. If $u$ is an element of $\mathcal{S}$, say $u = u_i$ , then $\mathcal{S} \backslash \{u_i\}$ is independent, and so we can choose $\mathcal{V}' \subseteq \mathcal{V}$ of size $n-k+1$ so that $\mathcal{S} \backslash \{u_i\} \cup \mathcal{V}'$ is again linearly independent but also spans $\mathcal{R}^n$. But then

$$\mathcal{S}' := \mathcal{S} \backslash \{u_i\} \cup \mathcal{V}' \cup \{u'\}$$

is a new simplex of $\mathcal{H}'$. Moreover, the map $\mathcal{S} \to \mathcal{S}'$ is one-to-one, and hence $simp(\mathcal{H}') \geq simp(\mathcal{H})$ as desired.

Thus $simp(\mathcal{H})$ is maximal when any $n$ element of $\mathcal{H}$ are linearly independent.

We now show that no other configuration may have so many simplexes.

For this, let $\mathcal{S} \subseteq \mathcal{H}$ be a fixed simplex of $\ell$ element. Using the above construction repeatedly $m - \ell$ many times, we can assume that no vector $u$ of $\mathcal{H}'\backslash\mathcal{S}$ belongs to any subspace generated my $n-1$ elements of $\mathcal{H}\backslash\{u\}$.

However it is now easy to obtain an upper bound for the number of simplexes in $\mathcal{H}$ : indeed we have $\mathcal{S}$ itself which is preserved and then there are only $n+1$ element simplexes which must contain at most $\ell - 1$ elements of $\mathcal{S}$ . That is

$$simp(\mathcal{H}) \leq 1 + \sum_{i=0}^{\ell-1} \binom{\ell}{i} \cdot \binom{m-\ell}{n+1-i} = 1 + \binom{m}{n+1} + \binom{m-\ell}{n+1-\ell} \quad .$$

But this quantity is strictly less than $\binom{m}{n+1}$ whenever $n+2 \leq m$.

For $m = n$, there are no simplexes and for $m = n+1$ there is a configuration with exactly one $k$ -simplex for every $2 \leq k \leq n+1$ .

This completes the proof. ■

**Corollary 4.4** *For any $\mathcal{H} \subset \mathbb{R}^n$ of fixed size (so that $\mathcal{H}$ spans $\mathbb{R}^n$) we have*

$$simp(\mathcal{H}) \leq \binom{m}{n+1} \quad . \qquad \square$$

## 4.2 The minimum case with parallel vectors

In this section we give a lower bound for the number of simplexes contained in a given collection of vectors $\mathcal{H} \subseteq \mathbb{R}^n$ of fixed size. We show that this bound is sharp when we allow parallel vectors in $\mathcal{H}$, namely we provide a construction which attains this minimal number of simplexes for each prescribed size of $\mathcal{H}$. It turns out that, however, that this construction is not unique, if we allow parallel vectors in $\mathcal{H}$.

The Theorem below summarizes our results:

**Theorem 4.5** *For any $\mathcal{H} \subseteq \mathbb{R}^n$ of fixed size so that $\mathcal{H}$ spans $\mathbb{R}^n$, $simp(\mathcal{H})$ is minimal if $\mathcal{H}$ consists of $n$ linearly independent equivalence classes of sizes differing by at most one from each other, where each equivalence class is a set of parallel vectors.*

*In case $\mathcal{H}$ contains no large simplexes, the minimal configuration is unique.*

**Proof.** From now on fix $n$ and $m$ and consider a collection $\mathcal{H} \subseteq \mathbb{R}^n$ of size $m$ which also spans $\mathbb{R}^n$ and for which $simp(\mathcal{H})$ is minimal. Clearly $m \geq n$.

Let $\theta_1, ..., \theta_p \subseteq \mathcal{H}$ be the distinct collections (equivalence classes) of parallel vectors of $\mathcal{H}$, and abusing notation, let $\theta_1, ..., \theta_p$ be members of each class, which we use as representatives of the classes. We shall also use $\theta_i$ to denote $|\theta_i|$ , the size of the collection represented by $\theta_i$ . Recall further that we call a simplex *large* if it contains at least 3 elements, otherwise it is *small*, and $[\mathcal{S}]$ denotes the *spanned subspace* of $\mathcal{S}$ for any set of vectors $\mathcal{S} \subset \mathbb{R}^n$.

For going on we need two lemmas before. ■

**Lemma 4.6** *If $\mathcal{H}$ contains a minimal number of simplexes, then*

***(i)*** *all vectors contained in large simplexes are contained in no other simplex and, especially, large simplexes are disjoint;*

***(ii)*** *we may assume that $\mathcal{H}$ has no large simplexes at all.*

**Proof. (i)** Let

$$\mathcal{H} = \bigcup_{i=1}^{p} \theta_i$$

and suppose that $\mathcal{H}$ contains a *large* simplex $\mathcal{S}$ , this forces $p \geq n+1$ . By relabeling, we may assume that $\theta_1$ and $\theta_2$ are members of $\mathcal{S}$ and that actually

$$\mathcal{S} = \{\theta_i : i \in \mathcal{I}\}$$

where $|\mathcal{I}| \geq 3$ .

We define now

$k :=$ the number of large simplexes that contain both $\theta_1$ and $\theta_2$ ,
$k_1 :=$ the number of large simplexes containing $\theta_1$ but not $\theta_2$ ,
$k_2 :=$ the number of large simplexes containing $\theta_2$ but not $\theta_1$

and suppose without loss of generality that $k_1 \geq k_2$ .

Take note now that

$$k \geq \prod_{i \in \mathcal{I} \setminus \{1,2\}} \theta_i \quad .$$

Now we form $\mathcal{H}'$ by deleting all elements of the collection $\theta_1$ and replacing each of them by a new vector in the collection of $\theta_2$ . Observe that $\mathcal{H}'$ still spans $\mathbb{R}^n$ as $\theta_1$ was a linear combination of the other members of any large simplex containing it. Further, this modification only affects the simplexes containing at least one member of $\theta_1$ or $\theta_2$ .

Before this modification, $\mathcal{H}$ contained

$$\binom{\theta_1}{2} + k_1\theta_1 + \binom{\theta_2}{2} + k_2\theta_2 + k\theta_1\theta_2$$

many simplexes containing a member of either $\theta_1$ or $\theta_2$ .

After this construction, $\mathcal{H}$ will have

$$\binom{\theta_1+\theta_2}{2} + k_2(\theta_1+\theta_2)$$

of such simplexes. The remaining simplexes are unchanged.

By minimality of $simp(\mathcal{H})$ , we must have

$$\binom{\theta_1}{2} + k_1\theta_1 + \binom{\theta_2}{2} + k_2\theta_2 + k\theta_1\theta_2 \leq \binom{\theta_1+\theta_2}{2} + k_2(\theta_1+\theta_2)$$

which, after an elementary calculation, reduces to

$$k_1 - k_2 \leq \theta_2(1-k)$$

and therefore $k = 1$ (as $k \geq 1$) and $k_1 = k_2$ . Thus

$$1 = k \geq \prod_{i \in \mathcal{I}\setminus\{1,2\}} \theta_i$$

which forces (by symmetry) that $\theta_i = 1$ for each $i \in \mathcal{I}$ .

But now, if a vector $v$ belongs to two different *large* implexes $\mathcal{S}_1$ and $\mathcal{S}_2$, then

$$(\mathcal{S}_1 \cup \mathcal{S}_2)\setminus\{v\}$$

is a linearly dependent collection on non-parallel vectors which therefore must contain a large simplex $\mathcal{S}'$. But $\mathcal{S}'$ must contain at least 2 element from either $\mathcal{S}_1$ or $\mathcal{S}_2$ which contradicts to the previous paragraph, i.e. to $k = 1$. This proves the first part of the Lemma.

**(ii)** Finally, without changing $simp(\mathcal{H})$ , we may replace one vector of a large simplex $\mathcal{S}$ by one parallel to another member of $\mathcal{S}$ which in effect replaces a large simplex of $\mathcal{H}$ by a 2-simplex, and $\mathcal{H}$ still spans $\mathbb{R}^n$.

This completes the proof of the Lemma. ■

Now we turn to vectors contained *only* in "small" simplexes, ie. in pairs of parallel vectors.

**Lemma 4.7** *If* $|\mathcal{H}| = m$ , $simp(\mathcal{H})$ *is minimal and* $\mathcal{H}$ *contains only small simplexes, then all vectors must belong to a collection of parallel vectors of sizes differing by at most 1.*

**Proof.** By the previous Lemma, we can assume that $\mathcal{H}$ contains no large simplex. Obviously, each collection $\theta_i$ of parallel vectors accounts for $\binom{\theta_i}{2}$ such simplexes.

If $\theta_i > \theta_j + 1$ , then putting one vector from $\theta_i$ to $\theta_j$ decreases the number of simplexes in $\mathcal{H}$ as shows the inequality

$$\binom{\theta_i}{2} + \binom{\theta_j}{2} > \binom{\theta_i - 1}{2} + \binom{\theta_j + 1}{2} \quad . \tag{4.2}$$

This completes the proof of the Lemma. ■

Now we turn to the proof of the Theorem.

**Proof. of Theorem 4.5.**

Let us suppose that given a collection $\mathcal{H} \subseteq \mathbb{R}^n$ of size $m$ which spans $\mathbb{R}^n$ and for which $simp(\mathcal{H})$ is minimal and without large simplexes. Now we can write

$$\mathcal{H} = \bigcup_{i=1}^{n} \theta_i$$

and therefore, if $m = an + b$ where $0 \leq b < n$ (and $a \geq 1$), we have

$$simp(\mathcal{H}) = b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(\mathcal{H})$$

as desired. The strict inequality (4.2) in the last Lemma shows that this configuration is unique when $\mathcal{H}$ contains no large simplexes. ■

From the above results one can easily deduce the *minimal number* of simplexes:

**Corollary 4.8** *Assuming $\mathcal{H} \subseteq \mathbb{R}^n$ spans $\mathbb{R}^n$ and $\mathcal{H}$ has size $m$ , and $m = an + b$ where $0 \leq b < n$ (and $a \geq 1$), then we have*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(\mathcal{H}) \quad . \qquad \square \tag{4.3}$$

As we indicated, the minimal configuration is not unique, more precisely when allowing large simplexes. For example, for $n + 1 \leq m < 2n - 1$ we have other constructions for achieving the lower bound in (4.3), as well:

**Example 4.9** *Let $\mathcal{K} = \{e_1, ..., e_n\} \subset \mathbb{R}^n$ a fixed base and let*

$$\{\mathcal{I}_1, ..., \mathcal{I}_k\} \subseteq \mathcal{P}(\{1, ..., n\})$$

*be a partition of the index-set* $\{1, ..., n\}$ *where each partition class* $\mathcal{I}_j$ *has size at least* 2 *, i.e.* $k < \frac{n}{2}$ *. Let further the vectors*

$$v_j := \sum_{i \in \mathcal{I}_j} \mu_i e_i \qquad (j \leq k)$$

*be arbitrary elements of the subspaces*

$$L_j := [\{e_i : i \in \mathcal{I}_j\}] \subset \mathbb{R}^n$$

*such that no* $\mu_i$ *might be* 0 *. Then, by Lemma 2.5 all the sets*

$$\{e_i : i \in \mathcal{I}_j\}$$

*are simplexes. This means, that the vectorset*

$$\mathcal{H} = \{e_1, ..., e_n\} \cup \{v_1, ..., v_k\}$$

*has* $n + k$ *elements and* $k$ *many large simplexes.* □

Using the results of Theorems 4.3 and 4.5 we easily can summarize our *quantitative* results as:

**Corollary 4.10** *Assuming* $\mathcal{H} \subseteq \mathbb{R}^n$ *spans* $\mathbb{R}^n$ *and* $\mathcal{H}$ *has size* $m$ *, and* $m = an + b$ *where* $0 \leq b < n$ *(and* $a \geq 1$*), then we have*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(\mathcal{H}) \leq \binom{m}{n+1} \quad . \qquad \square \qquad (4.4)$$

Unfortunately these bounds are far from each other, but both of them are strict. Only the lower bound can be raised with certain assumption: excluding parallel elements, or more generally: excluding small simplexes. These cases are discussed in the forthcoming Section, in Chapter 5 "*Matroids*" and in Chapter 7 "*Beyond the thesis*".

## 4.3 The minimum case without parallel vectors in $\mathbb{R}^3$

In this section we completely describe the more appropriate problem of how to obtain the minimal number of simplexes in $\mathbb{R}^3$, allowing **no** collinear vectors among our given vectors.

**Theorem 4.11** *For any $\mathcal{H} \subseteq \mathbb{R}^3$ of fixed size not equal to 3, 4 or 7 such that $\mathcal{H}$ spans $\mathbb{R}^3$ and contains **no** collinear vectors, $simp(\mathcal{H})$ is minimal if and only if $\mathcal{H}$ is contained in two intersecting planes, one of which is of size 3; i.e. precisely when $\mathcal{H}$ contains three linearly independent vectors $\{u_1, u_2, u_3\}$, another vector $v$ coplanar with $u_1$ and $u_2$ and the rest $\mathcal{H}\backslash\{u_1, u_2, u_3, v\}$ coplanar with $u_2$ and $u_3$ .* $\square$

(Since the proof of the above Theorem is fairly long, we only refer to [$SzL98$] where the reader can find all details.)

For $|\mathcal{H}| = 3$, $\mathcal{H}$ must consist of 3 linearly independent vectors as it is required to span $\mathbb{R}^3$, and therefore $simp(\mathcal{H}) = 0$ .

For $|\mathcal{H}| = 4$, there are 2 optimal configurations with 1 simplex, these constructions are displayed in Figure 4.1.

Here and for all subsequent figures, points represent vectors, and aligned points represent vectors in the same plane.

Figure 4.1: *Two optimal configurations for $|\mathcal{H}| = 4$*

For $|\mathcal{H}| = 7$, the analysis contained in this paper will provide the required tools for the reader to verify that there are 3 optimal configurations with 17 simplexes (one of which is contained in 6 planes each of size 3), as Figure 4.2 displays them.

Theorem 4.11 easily implies the following bounds for the number of simplexes:

**Corollary 4.12** *Let $\mathcal{H} \subseteq \mathbb{R}^3$ such that $\mathcal{H}$ spans $\mathbb{R}^3$, $|\mathcal{H}| = m \geq 4$ and $\mathcal{H}$ contains no collinear vectors. Then we have:*

$$\binom{m-2}{3} + 1 + \binom{m-3}{2} \leq simp(\mathcal{H}) \leq \binom{m}{4} \quad . \qquad \square$$

Figure 4.2: *Three optimal configurations for* $|\mathcal{H}| = 7$

The general problem in $\mathbb{R}^n$ regarding the minimum size of $simp(\mathcal{H})$ where $\mathcal{H}$ is of fixed size, spans $\mathbb{R}^n$ and contains **no** collinear vectors remains *open*. However we have a conjecture that the minimum is attained precisely in certain configurations, details are explained in Conjecture 7.2 in Chapter 7 "*Beyond the thesis*".

# Chapter 5

# Matroids

In this Chapter we investigate the maximum and minimum number of bases and circuits in a matroid and their structure. These problems are natural generalizations of the concept "simplexes" and the problems in the previous Chapter.

## 5.1 Introduction

Recall that the (linear algebraic and not geometric) *simplexes* in $\mathbb{R}^n$ are any sets of vectors $S \subset \mathbb{R}^n$ such that $S$ itself is linearly dependent but all its proper subsets are independent. This notion does not use the usual operators $+$ and $\cdot$ of vectors of $\mathbb{R}^n$ but only the relation *independence* among them. (We could substitute $\mathbb{R}^n$ to any finite dimensional linear space, of course.) The general structures *matroids* deal with this relation *independence* only. Moreover, these structures are common generalizations of linear spaces, graphs, set systems, partitions, etc., so any result on matroids has many corollaries for these latter structures. (Exhaustive investigations of matroids can be found eg. in Recski's [$R89$] or Oxley's [$O92$] books.)

For an arbitrary matroid, the corresponding notion of a simplex is called a **circuit**, that is *a dependent set all of whose proper subsets are independent.* Now the corresponding generalized problem is the following:

*" What is the minimum and maximum number of circuits and bases in matroids of given size and rank and what are the extremal configurations? "*

We completely solve the maximum case and partially answer the minimum case, where the exact value of the lower bound remains open when neither parallel elements nor loops are allowed in the matroid.

Let us highlight again that the **main question** is to determine the extremal configurations, the maximal number of circuits and bases is a not too hard combinatorial question using Sperner's theorems.

Despite of ours and others' intensive search for relevant literature, only Murty's paper [$M71$] on equicardinal matroids (where all circuits have the same size) was found.

The matroid terminology used here fits to Recski's [$R89$], Oxley's [$O92$] or to the author's [$Sz01n$] works.

**Definition 5.1** *Let $X$ be an arbitrary nonempty set and let $\mathcal{F} \subseteq P(X)$ any system of subsets of $X$. Now the structure $\mathcal{M} = (X, \mathcal{F})$ is called a* ***matroid*** *if the following properties hold:*

***(I1)*** $\emptyset \in \mathcal{F}$

***(I2)*** *$y \in \mathcal{F}$ and $x \subseteq y$ imply $x \in \mathcal{F}$ ($\mathcal{F}$ is* ***descending****)*

***(I3)*** *for any set $x \subseteq X$ the maximal subsets of $x$ belonging to $\mathcal{F}$ have the same size (depending only $x$).*

*The members of $F$ are called* ***independent*** *subsets of $S$.* □

$X$ is called the **ground set** of $\mathcal{M}$ and $\mathcal{F}$ is the set of **independent** subsets of $X$. We usually use **m** for the size of the matroid, i.e. the cardinality of $X$, and **n** for its rank $n$, i.e. the cardinality of any base of $\mathcal{M}$. We assume that $0 < n < m$, as the case $m = n$ is trivial. Through this note we use the following convenient notion:

**Definition 5.2** *A circuit is called* ***small*** *if it consists of at most 2 elements. A circuit will be called* ***large*** *if it contains at least 3 elements.* □

Our main results in this Chapter are listed in the series of the Theorems 5.3, 5.5, 5.6, 5.7, 5.11, 5.12, 5.13, 5.19 and 5.21.

## 5.2 On the maximum

In this Section we count the *maximum* number of circuits and bases in matroids of size of $m$ and rank $n$, exhibiting the unique structure of the resulting matroids.

### 5.2.1 Maximum number of circuits

Our results in this section can be summarized in the following Theorem:

**Theorem 5.3** *If $m > n+1$, then only the uniform matroid $U_{m,n}$ contains the maximum number of circuits, $\binom{n+1}{m}$. If $m = n+1$, all matroids of size $m$ and of rank $n$ contain exactly 1 circuit.*

**Proof.** To prove Theorem 5.3 we first describe *Construction 1* for building a new matroid $\mathcal{M}' = (X', \mathcal{F}')$ from any matroid $\mathcal{M} = (X, \mathcal{F})$.

**Construction 1:** Let $u$ be an element of $X$ . Then $\mathcal{M}'$ is obtained by freely adding a new element $u'$ to $\mathcal{M}\backslash u$. [See Oxley's book, [O], Section 7.2.] Note that

$$X' := X\backslash\{u\} \cup \{u'\}$$

and

$$\mathcal{F}' := \{f \in \mathcal{F} : f \subseteq X\backslash\{u\}\} \cup \{f \cup \{u'\} : f \in \mathcal{F},\ f \subseteq X\backslash\{u\}, \mid f \mid \leq n-1\} \quad .$$

It is straightforward to verify that the size and rank are preserved, and that the new element $u'$ is not a member of any small circuits in $\mathcal{M}'$. More importantly, if an element of $X\backslash\{u\}$ is not contained in a small circuit of $\mathcal{M}$, then the same remains true in $\mathcal{M}'$. Further the number of circuits in $\mathcal{M}'$ is at least that of $\mathcal{M}$.

We continue our proof by the following Lemma: ■

**Lemma 5.4** *The number of circuits in $\mathcal{M}$ is strictly less than $\binom{n+1}{m}$ whenever $\mathcal{M}$ contains a small circuit and $m > n+1$.*

**Proof.** of the Lemma: Let $K \subseteq X$ be a fixed small circuit of $\ell$ elements, $\ell \leq n$. Using the above Construction 1 repeatedly $m-\ell$ times, we can replace each $u \in X\backslash K$ by a new element $u'$ as described. The number of circuits has not decreased and in fact the circuits left are $K$ itself and all other ones must be of size $n+1$. The number is therefore at most

$$1 + \sum_{i=o}^{\ell-1} \binom{\ell}{i}\binom{m-\ell}{n+1-i} = 1 + \binom{m}{n+1} - \binom{m-\ell}{n+1-\ell}$$

which is strictly less than $\binom{m}{n+1}$ iff $m > n+1$ . ■

Now we can conclude the proof of our Theorem.

**Proof. of Theorem 5.3.** For the case $m = n+1$ , we have a base $\{u_1, u_2, \ldots, u_n\}$ and therefore $S = \{u_1, u_2, \ldots, u_n, v\}$ contains a unique circuit. This concludes the proof of Theorem 2.1. ■

### 5.2.2 Bases

It turns out that the above *Construction 1* does not decrease the number of bases either, and again only $U_{m,n}$ does have the maximum number of bases, namely $\binom{m}{n}$ . We can assume that $m > n > 0$ and we consider a matroid $\mathcal{M} = (X, \mathcal{F})$ of size $m$ and rank $n$.

**Theorem 5.5** *Only the uniform matroid $U_{m,n}$ contains the maximum number of bases, namely $\binom{m}{n}$ .*

**Proof.** We first verify that the number of bases does not decreases during Construction 1, where an element $u \in X$ has been replaced by an element $u'$. Let $B \subseteq X$ be a base of $\mathcal{M}$. If $u \notin B$ then $B$ remains a base also in $\mathcal{M}'$; otherwise (if $u \in B$) $B \backslash \{u\} \cup \{u'\}$ is now a base in $\mathcal{M}'$.

This means that we have a one-to-one correspondence between the bases of $\mathcal{M}$ and some bases of $\mathcal{M}'$.

We now show that any matroid containing small circuits contains strictly less than $\binom{m}{n}$ bases. Let $\mathcal{M} = (X, \mathcal{F})$ be a matroid containing a small circuit $K$ of size $\ell$ where $\ell \leq n$. As before, replace all the elements $u$ of $X \backslash K$ repeatedly by a corresponding $u'$ as described in the Construction 1. In the final matroid the bases are exactly all the $n$-element subsets of $X$ not containing $K$. The number of these subsets is

$$\sum_{i=o}^{\ell-1} \binom{\ell}{i} \binom{m-\ell}{n-i} = \binom{m}{n} - \binom{m-\ell}{n-\ell}$$

which is clearly strictly less than $\binom{m}{n}$ using $\ell \leq n \leq m$ . ∎

## 5.3 On the minimum

In this Section we give a lower bound for the number of circuits and bases contained in a matroid of size $m$ and of rank $n$. As opposed to the maximum case, the answer here for the minimum case depends on whether we allow loops or parallel elements; subsections 5.3.1 and 5.3.2 investigate separately these cases. We again describe the unique (minimal) configurations. As in [$SzL95$] and in [$SzL98$], a third case excluding both loops and parallel elements remains *open*.

### 5.3.1 Allowing loops

In this subsection we analyze the minimum number of circuits and bases in matroids, allowing one element dependent sets, called *loops*. (These loops are necessarily circuits.)

We shall assume that $m > n$, since the trivial case $m = n$ implies that such a matroid would have *no* circuit and only *one* base.

**Theorem 5.6** *For each $m$ and $n$, there is a unique matroid $\mathcal{M}_o$ of size $m$ and of rank $n$ containing the minimal number of bases, namely 1, when we allow loops in the matroid.*

**Proof.** Let $\mathcal{M}_o := (X_o, \mathcal{F}_o)$ be the matroid of size $m$ and rank $n$ where

$$X_o = \{u_1, \ldots, u_n, v_1, \ldots, v_{m-n}\}$$

and $B = \{u_1, \ldots, u_n\}$ is the (only) basis, and $v_1, \ldots, v_{m-n}$ are loops, the only circuits of the matroid. (Note, that $B$ is the the unique basis in the matroid $\mathcal{M}_o$.)

We show now that any matroid but $\mathcal{M}_o$ contains more than one base. Observe that such a matroid $\mathcal{M}$ contains a circuit, say $K$, of more than one element.

Consider any element from $K \backslash B$. This element must be independent, by the definition of a circuit, and can therefore be extended it to a second base of $\mathcal{M}$ . ■

**Theorem 5.7** *Any matroid $\mathcal{M}$ of size $m$ and of rank $n$ contains at least $n - m$ circuits. A matroid contains exactly $m - n$ circuits if and only if the circuits of the matroid are pairwise disjoint.*

**Proof.** Consider a base $B$ of the matroid $\mathcal{M}$. For any $u \in X \backslash B$ the corollary of the weak axiom for circuits implies that there is a (unique) circuit containing $u$ included in $B \cup \{u\}$ . We conclude that $\mathcal{M}$ has at least $m - n$ many circuits. Now suppose that $\mathcal{M}$ contains exactly $m - n$ circuits. Fix a base $B$ of $\mathcal{M}$, and let $X \backslash B = \{v_1, v_2, \ldots, v_{m-n}\}$ . For each $1 \leq i \leq m - n$ there is a circuit $K_i \subseteq B \cup \{v_i\}$ . These circuits are different for $i \neq j$ since $K_i$ must contain $v_i$ , but $K_j$ does not contain it. If there were two intersecting circuits $K_i$ and $K_j$ containing a common element $u$, then, by the strong axiom for circuits, the set $K_i \cup K_j \backslash \{u\}$ would contain a circuit $K$, necessarily distinct from all circuits $K_\alpha$ $(1 \leq \alpha \leq m - n)$ which is a contradiction. ■

**Remark 5.8** *The matroid $\mathcal{M}_o$ defined above also contains exactly $m - n$ pairwise disjoint circuits, i.e. loops.*

### 5.3.2 Allowing parallel elements, no loops

As before, $\mathcal{M} = (X, \mathcal{F})$ denotes an arbitrary fixed matroid of size $m$ and of rank $n$. Recall that two elements are called parallel if together they form a circuit. In this subsection we determine the minimal number of circuits and bases in the case where $\mathcal{M}$ may not contain loops, but where parallel elements are allowed.

We describe a second construction to modify the matroid in order to reduce the number of bases and circuits. Using this construction we will describe the unique structures of matroids having the minimal number of circuits and bases.

**Construction 2:** Let $u_1 \in X$ be any fixed element such that, when deleting it from $X$, the rank does not decrease, ie. $r(X) = r(X \backslash \{u_1\}$. (For example, any element which is a member of a circuit has this property.)

Fix further a second arbitrary element $u_2 \in X$ and a new element $u' \notin X$. We now define the matroid $\mathcal{M}' := (X', \mathcal{F}')$ by

$$X' := X \backslash \{u_1\} \cup \{u'\}$$

and

$$\mathcal{F}' := \{f \in \mathcal{F} : f \subseteq X \backslash \{u_1\}\} \cup \{f \cup \{u'\} : f \cup \{u_2\} \in \mathcal{F},\ f \subseteq X \backslash \{u_1, u_2\}\}\ .$$

□

In practice, this second construction will be used when $u_1$ and $u_2$ are members of a common circuit. The effect is essentially that we delete $u_1$ from the matroid and add a new $u'$ parallel to $u_2$.

**Lemma 5.9** *$\mathcal{M}' = (X', \mathcal{F}')$ is again a matroid of size $m$ and of rank $n$.*

**Proof.** The size and rank of $\mathcal{M}'$ have not changed since $|X'| = |X| = m$, and since by Construction 2, $u_1$ was chosen so that its removal does not decrease the rank of $\mathcal{M}$. What must be verified carefully is that $\mathcal{M}'$ is a matroid, although only the so-called independence augmentation axiom requires a proof; that is we must show that if $f_1$ and $f_2$ are members of $F'$ with $|f_1| < |f_2|$ , then there is an element $e \in f_2 \setminus f_1$ such that $f_1 \cup e \in F'$. There are four cases, depending whether $u' \in f_i$ .

The only interesting case is when $u' \notin f_1$ and $u' \in f_2$ . This means that $f_1 \in F$ but $u_1 \notin f_1$ ; and if $f_2' = f_2 \setminus \{u'\}$ then $f_2' \cup \{u_2\} \in F$, $f_2' \subseteq S \setminus \{u_1, u_2\}$ .

But $|f_1| < |f_2' \cup \{u_2\}|$ and there is therefore an $e \in f_2' \cup \{u_2\} \setminus f_1$ such that $f_1 \cup \{e\} \in F$ . If $e = u_2$ then $f_1 \cup \{u'\}$ is as desired. If otherwise $e \neq u_2$ then $f_1 \cup \{e\}$ is good enough. ■

We are now ready to investigate the effect of this Construction 2 on the number of circuits and of bases.

### Circuits

In order to find the structure of the extreme minimal matroid, we investigate the effect of the above Construction 2 on the number of circuits, with a careful choice of the element $u_1$.

**Lemma 5.10** *Suppose that $u_1, u_2 \in X$ are contained in a same large circuit, and denote $k_i$ the number of circuits containing $u_i$ but not $u_j$ . If $k_1 \geq k_2$ , then deleting $u_1$ from $\mathcal{M}$ and adding a new element parallel to $u_2$ into $\mathcal{M}$ as in Construction 2 does not increase the number of circuits.*

**Proof.** Denote also by $k_{12}$ the number of circuits containing both $u_1$ and $u_2$, and as usual let $u'$ be the new element we just added to $\mathcal{M}$. Notice that exactly the circuits containing $u_1$ were deleted during the Construction 2, i.e. $k_1 + k_{12}$ many. We introduced new circuits, namely the two-element circuit $\{u_2, u'\}$ and the circuits now containing $u'$ instead of $u_2$ in $\mathcal{M}$ (but not $u_1$), we have $k_2$ many of them. Thus the number circuits is changed by $k_2 + 1 - k_1 - k_{12}$ , which is not positive since $k_1 \geq k_2$ and $k_{12} \geq 1$ . Moreover, the number of circuits remains unchanged iff $k_1 = k_2$ and $k_{12} = 1$. ■

Using Construction 2 repeatedly we eventually reach a matroid not containing any large circuits, only circuits consisting of two parallel elements. Therefore among this kind must be a matroid having the minimum number of circuits. The following Theorem say that all of matroids having the minimum number of circuits are among this kind.

**Theorem 5.11** *Suppose that there are no large circuit and no loops in the matroid $\mathcal{M}$ and let $\{a_1, a_2, \ldots, a_n\}$ be any fixed base. If $\vartheta_i$ denotes the number of elements in $\mathcal{M}$ parallel to $a_i$ (including $a_i$ itself) for $i = 1, 2, \ldots, n$ then $\mathcal{M}$ contains the minimum number of circuits iff*

$$|\vartheta_i - \vartheta_j| \leq 1 \qquad \text{for } i \neq j \quad .$$

**Proof.** It is not difficult to verify that the assumptions on $\mathcal{M}$ together with the weak axiom for circuits imply that every element of $X$ is parallel to one and exactly one of the $a_i$ 's, and therefore

$$\sum_{i=1}^{n} \vartheta_i = m \quad .$$

Suppose on the contrary that $\vartheta_j > \vartheta_\ell + 1$ for some $j, \ell \leq n$ . Delete $a_j$ and add an element parallel to $a_\ell$, as in the above Construction 2. Since there are no large circuits in our matroid, the number of circuits in $\mathcal{M}$ is

$$\binom{\vartheta_j}{2} + \binom{\vartheta_l}{2} + \sum_{i \neq j,\ell} \binom{\vartheta_i}{2}$$

which becomes in $\mathcal{M}'$

$$\binom{\vartheta_j - 1}{2} + \binom{\vartheta_\ell + 1}{2} + \sum_{i \neq j,\ell} \binom{\vartheta_j}{2} \quad .$$

These expressions clearly show that the number of circuits did strictly decrease.

Defining a relation on $X$ by

$$b \sim c$$

**iff** they are parallel to the same $a_i$ is an equivalence relation, we obtain that a matroid as above contains the minimal number of circuits exactly in the case when the equivalence classes of parallel vectors have almost all the same size, i.e. differing by at most one. ■

**Corollary 5.12** *The minimum number of circuits in a matroid of size $m$ and of rank $n$ , where $m = an + b$ , $0 \leq b < n$ , is*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$$

*and in particular, if $m$ is a multiple of $n$,*

$$n \cdot \binom{\frac{m}{n}}{2} \quad . \qquad \square$$

Now we turn to the exact *structure* of the matroids containing the minimal number of circuits. We will see that for small matroids there are more possibilities while the structure of large matroids are unique.

**Theorem 5.13** ***a)*** *For $m < 2n$ , a matroid of size $m$ and rank $n$ contains the minimal number of circuits iff all its circuits are disjoint.*

***b)*** *For $m \geq 2n$ , a matroid contains the minimal number of circuits iff it contains only 2-element circuits (i.e. parallel elements), and the sizes of the equivalence classes of parallel elements differ by at most 1 .*

Let us note, that there are many matroids satisfying a) while the matroids described in b) are, in fact, isomorphic.

The *proof* of the above theorem is based upon the following lemmas.

**Lemma 5.14** *If $\mathcal{M}$ contains two large circuits $K$ and $L$, then*

$$|K \cap L| \leq 1 \quad .$$

**Proof.** If $K \cap L$ contains two distinct elements $u_1 \neq u_2$ then the proof of Lemma 5.10, using $k_{12} \geq 2$ shows that $\mathcal{M}$ does not contain the minimal number of circuits. ■

**Lemma 5.15** *Let $K$ be a large circuit and let $u \notin K$ be arbitrary. Then either $u$ is parallel to some element of $K$, or else $u$ is not contained in any large circuits intersecting $K$.*

**Proof.** Suppose that $L$ is a large circuit containing $u$ and intersecting $K$. Using Lemma 5.14, we must have exactly one element in $K \cap L$, say $v$.

Then, by the strong axiom of circuits of matroids, there is a circuit $H \subseteq K \cup L \backslash \{v\}$ containing $u$.

If $H$ is large, then at least one of the two sets $H \cap L$ and $H \cap K$ has at least two elements, contradicting the previous Lemma.

If $H$ is small, then $u$ must be parallel to an element of $K$.

This completes the proof. ■

**Lemma 5.16** *No element of a large circuit can be parallel to any element of the matroid.*

**Proof.** Consider a large circuit $K = \{u_1, u_2, \ldots, u_p\}$ (i.e. $p \geq 3$). Suppose on the contrary that an element of $K$, say $u_1$, is parallel to some other element $u_1' \neq u_1$. We claim that $K' = \{u_1', u_2, \ldots, u_p\}$ is again a large circuit, contradicting Lemma 5.14. If $K' \in \mathcal{F}$, then we could extend it to a base $B$, but now $B \cup \{u_1\}$ would contain the distinct circuits $K$ and $\{u_1, u_1'\}$, contradicting the weak axiom for circuits. However every proper subset of $K'$ does belong to $\mathcal{F}$; indeed otherwise such a subset must contain a circuit $L$, which cannot be large by Lemma 5.14 again. But $L$ cannot be a two-element circuit since $u_1'$ is parallel to $u_1$. ■

The above lemmas imply that each large circuit must be disjoint from every (large or small) circuit in $\mathcal{M}$. Now it remains to consider small circuits.

**Lemma 5.17** *If $\mathcal{M}$ contains a large circuit, then there are no three pairwise parallel elements in $\mathcal{M}$.*

**Proof.** Let $K$ be a large circuit and suppose that three pairwise parallel elements exist in $\mathcal{M}$. By Lemma 5.16, we may assume that none of these three elements belong to $K$. Let $u_1$ be one of these three elements and let $u_2$ be any element of $K$. Use once again Construction 2 to delete $u_1$ and add a new element $u_2'$ parallel to $u_2$; this is possible as $\mathcal{M}$ is assumed to contain no loops and therefore $u_1$ satisfies the hypothesis for the Construction. Using a calculation similar to Lemma 5.10 and the same notation, we have $k_2 = 1$ since $K$ is the only circuit containing $u_2$ . $k_1 \geq 2$ since we have at least two elements parallel to $u_1$, and finally $k_{12} = 0$ since $u_1$ is not contained in any large circuit intersecting $K$ by Lemma 5.15 and is not parallel to any element of $K$ by Lemma 5.16 Therefore, during the Construction 2, we deleted $k_1$ circuits; we added the circuit $\{u_2, u_2'\}$ of course as well as the circuit $K \backslash \{u_2\} \cup \{u_2'\}$ . Thus the number of circuits has changed by $1 + 1 - k_1 \leq 0$ , so this number certainly did not increase. But now we can use the procedure described in Lemma 5.16 to decrease the number of circuits. This contradiction shows that $\mathcal{M}$ was not minimal. ■

Now we can turn to the proof of Theorem 5.13.

**Proof. of Theorem 5.13.**

The above results show that all circuits in $\mathcal{M}$ must be disjoint in the presence of a large circuit. In this case fix any base $B$ of $\mathcal{M}$. For each element $u$ of $S \setminus B$ , $B \cup \{u\}$ must contain a circuit, which in turn must contain at least one element of $B$ . Since all circuits are assumed to be pairwise disjoint, $S \setminus B$ can contain at most $n$ elements. Therefore for $m \geq 2n$ , a matroid with the minimum number of circuits cannot contain any large circuit. In the lack of large circuit, using Theorem 5.11, the equivalence classes of parallel elements must have almost the same size. This implies the statement of Theorem 5.13. ■

**Remark 5.18** *The last part of the above proof describes uniquely the structures of matroids containing the minimal number of circuits when $m \geq 2n$.*

## BASES

The structure of matroids containing the minimal number of bases is always unique, as described in the following Theorem.

**Theorem 5.19** *A matroid $\mathcal{M}$ of size $m$ and rank $n$ contains the minimal number of bases iff it has a base $\{a_1, a_2, \ldots, a_n\}$ such that all other elements in $\mathcal{M}$ are parallel to $a_1$ .*

As in the previous subsection, we use Construction 2 to achieve the minimal number of bases. The following result describes the effect of this construction on the number of bases.

**Lemma 5.20** *Let $K$ be a large circuit in $\mathcal{M}$ and let $u_1, u_2 \in K$ . Denote by $\ell_1$ the number of bases containing $u_1$ but not $u_2$, and similarly for $\ell_2$. Then deleting $u_1$ and adding a new element parallel to $u_2$ (as in Construction 2), the number of bases strictly decreases whenever $\ell_1 \geq \ell_2$ .*

**Proof.** Denote by $\ell_{12}$ the number of bases containing both $u_1$ and $u_2$. By deleting $u_1$, we loose exactly the bases containing $u_1$ , that is $\ell_1 + \ell_{12}$ many of them. By adding a new element to $\mathcal{M}$ parallel to $u_2$, we gain $\ell_2$ many new bases. Clearly the set $\{u_1, u_2\}$ is independent since $K$ is assumed to be a large circuit, so it can be extended to a base, which implies $\ell_{12} \geq 1$ . This, together with $\ell_1 \geq \ell_2$ means that the number of bases strictly decreases. ■

Using the above result, we can remove each large circuit of the matroid while decreasing the number of bases. In other words, the matroids containing the minimal number of bases do not contain any large circuit. This means that we are able to prove Theorem 5.19.

**Proof. of Theorem 5.19.** Suppose that $\mathcal{M}$ does not contain any large circuit, and let $B = \{a_1, a_2, \ldots, a_n\}$ be any fixed base of $\mathcal{M}$ . By adding any other element $u$ to this set, we obtain the collection $B \cup \{u\}$ which must contain a circuit, and therefore $u$ must be parallel to one of the base elements $a_i$, since $\mathcal{M}$ does not contain large circuits.

Denote $k_i$ the number of elements from $X \backslash B$ parallel to $a_i$ (including $a_i$ itself); clearly $\sum_{i=1}^{n} k_i = m$ . Now the number of bases (picking an element from each equivalence class) is

$$\prod_{i=1}^{n} k_i \quad .$$

But in the case $k_\ell \geq k_j \geq 2$ , we can delete an element parallel to $a_j$ and add a new element to $\mathcal{M}$ parallel to $a_\ell$ ; the number of bases changes to

$$\prod_{i \neq j,\ell}^{n} k_i \cdot (k_j - 1) \cdot (k_\ell + 1)$$

which is strictly less. This implies that all but one $k_i$ equals to 1 . ■

**Corollary 5.21** *The minimal number of bases is $m - n + 1$ , and the minimal configuration is unique.* □

Despite our above results, the structural and quantitative properties of the matroids with extreme quantity of bases or loops, containing neither loops nor parallel elements, is *open.*

**Problem 5.22** *Characterize the matroids with the minimal number of circuits and bases, when neither parallel elements or loops are allowed.*

We discuss this question in some more detail in Chapter 7 "*Beyond the Thesis*" .

# Chapter 6

# The valuation operator

Using the ideas explained in the introductory Chapters 1 and 2 we interpret the vectors of the $n$ -dimensional Euclidean space $\mathbb{R}^n$ in several ways as species (groups of atoms), reactions, mechanisms, measure units, etc. Now then any linear (additive and homogeneous) quantity (chemists call them *valuation operators*) of any of these interpretations is, in fact a linear functional $\mathcal{L} : \mathbb{R}^n \to \mathbb{R}$. Many examples, practical methods and even applications are described for example also in [$RS66$] or in Pethő's works, widely used already in practice and are called *estimation and correlation methods of thermodynamic parameters* in thermodynamics and thermophysics.

Using the theory of linear functionals (esp. the Representation Theorem of F. Riesz) we can investigate the structure of these linear functionals and may draw further conclusions.

We presented a theoretical investigation and background for calculation methods already in use concerning valuation operators (increments/ linear functionals/ quantitative characteristics) in several fields of chemistry and physics.

As direct consequences we prove e.g. that linear increments can really be computed as weighted sum of the increments of the components (see (6.3) in Corollary 6.5), or we presented a one-sentence proof of Hess' law in thermochemistry in (6.5), we gave estimates for the magnitude of $\mathcal{L}(S)$ in (6.8), etc.

## 6.1 Vectors

Below we shortly list again stoichiometrical and physical *examples* which we can interpret with vectors of $\mathbb{R}^n$ and just after we connect them with linear quantites in order to illustrate our general ideas which will be explained in

the next Section.

**a) Species:** if the species (either active or chemical or groups of atoms only) $A_1, ..., A_n$ consist of the atoms $E_1, ..., E_m$ as $A_j = \sum_{i=1}^{m} a_{i,j} E_i$ where $a_{i,j} \in \mathbb{N}$ for $j = 1, ..., n$ and $i = 1, ..., m$, and the set $\{E_1, ..., E_m\}$ is fixed, we can assign to the species $A_j$ the *vectors*[1]

$$\underline{\mathbf{A}}_{\mathbf{j}} := [a_{1,j}, a_{2,j}, ..., a_{m,j}]^T \in \mathbb{R}^m$$

or in other words $\underline{A}_j = \sum_{i=1}^{m} a_{i,j} \underline{E}_i$ for $j = 1, ..., n$ assuming that $\{\underline{E}_1, ..., \underline{E}_m\} \subseteq \mathbb{R}^m$ is a (natural) base in $\mathbb{R}^m$.

We can use the same model when the components $E_1, ..., E_m$ denote (functional) groups of atoms which is widely used in practice.

The *molar volume* of species is usually computed as the sum (i.e. linear combination) of the components' data. This is a typical example where we can assume that the molecular quantitative property (increment) can be added linearly from the amount of that property (increment) of the components (functional groups or bonds). Other examples are the *enthalpy of formation* or the *heat capacity.*

**b) Reactions:** if we are given the reactions $X_1, ..., X_k$ which use the (fixed set of) species $A_1, ..., A_n$ as $X_j = \sum_{i=1}^{m} b_{i,j} \cdot A_i$ then we can correspond to these reactions the vectors $\underline{\mathbf{X}}_j := [b_{1,j}, \ldots, b_{n,j}]^T \in \mathbb{R}^n$, i.e. $\underline{\mathbf{X}}_j = \sum_{i=1}^{m} \mathbf{b}_{i,j} \cdot \underline{\mathbf{A}}_i$ where $b_{i,j} \in \mathbb{Z}$ for $j = 1, ..., k$ and $i = 1, \ldots, n$ if the base vectors were be chosen to $\underline{A}_1, ..., \underline{A}_n \in \mathbb{R}^n$ .[2]

The *standard Gibbs free energy change* $\Delta G^o$ (or free entalpy) of a reaction is the sum (linear combination) of the standard chemical potencials $\mu_i$ of the components (species) involved in the reaction as

$$\Delta G^o = \sum_{i=1}^{n} \nu_i \mu_i^o \quad .$$

The *heat of reactions* when studying mechanisms: Hess' wellknown law states that the resulting heat is again the sum (linear combination) of the heat of single reactions taking part in the mechanism. (This example is studied in [*P*93] and in [*P*95].)

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[1] We do not emphasize the difference between the species $A_j$ and the vectors $\underline{A}_j$ .

[2] Moving the terms with negative coefficients $b_{i,j}$ to the left-hand side of the equality (initial materials of the reaction) and leaving the others in the right-hand side (resulting materials) we get the usual form of the mechanism.

**c) Mechanisms:** any linear combinations of (the fixed set of) reactions $\{X_1,\dots , X_k\}$ are called mechanisms, and similarly we can assign these mechanisms $\mathcal{M}_t = \sum_{j=1}^{k} \lambda_{t,j} \cdot X_j$ to the vectors $\underline{\mathbf{m}}_t := [\lambda_{t,1}, \dots , \lambda_{t,k}]^T$, i.e. $\underline{\mathbf{m}}_t = \sum_{j=1}^{k} \boldsymbol{\lambda}_{t,j} \cdot \underline{\mathbf{X}}_j \in \mathbb{R}^k$ where of course $\lambda_{t,j} \in \mathbb{Z}$ for $t = 1, \dots , \ell$ and $j = 1, \dots , k$ .[3] The base in this case, is $\{\underline{X}_1, ..., \underline{X}_k\} \subset \mathbb{R}^k$.

**d) Measure units:** every (composite) measure unit $M_1, \dots , M_n$ is built up from elementary units $E_1, \dots , E_m$ (such as lenght, mass, time, etc.) as $M_i = \prod_{j=1}^{m} E_j^{a_{i,j}}$ where $a_{i,j} \in \mathbb{Z}$ for $i = 1, \dots , n$ and $j = 1, \dots , m$. Clearly we again can assign the measure units $M_i$ to the *vectors* $\underline{M}_i := [a_{i,1}, \dots , a_{i,m}]^T \in \mathbb{R}^m$ since any *product* of the powers of the units $M_i$ correspond to a linear combination of the vectors $\underline{M}_i$ (see e.g. the Reynold's numbers).

For properties which are not linear but multiplicative instead, as in the present example, we can use the logarithm function for getting linear correspondance – among the logarithm of the property of the parts, as we did in example *d*) in Section 2 (see also [*P*90]) or is applied eg. in [*MK*] for drawing Pourbaix diagrams.

One could find many more such examples (e.g.how atoms are built up from atomic parts) where our theory below could also be applied.

Clearly the long list could be continued up to infinity.

## 6.2 Mathematical formulation

Let us remark that we have to fix the set of building **components** (atoms/ species/ reactions) to build more complicated **structures** (as species/ reactions/ mechanisms) *in advance* since this set gives not only the base of the space but the dimension or even the space itself in which our investigations take place. For our further reference we fix these concept into a precise definition.

**Definition 6.1** *All the elements of an arbitrary but fixed and finite set*

$$\{C_1, \dots , C_N\}$$

*are called* ***components****, and any (possibly only formal) linear combination*

$$\underline{S} = \sum_{i=1}^{N} s_i \cdot C_i$$

[3] Negative coefficients mean that the corresponding reactions take place in reverse order.

*of its elements with arbitrary real numbers* $s_i \in \mathbb{R}$ *are called* ***structures***. □

At the end of this Chapter we discuss the case of *subsequent adding* new structures containing new components, i.e. how to extend the dimension of the space we are in and how to continue the calculations in the extended space without giving up our old results.

Next, we call any linear mapping of real value (i.e.a linear functional) which maps from (the above) structures a *valuation operator*.

**Definition 6.2** *Any linear mapping (or functional)* $\mathcal{L} : \mathbb{R}^n \to \mathbb{R}$ *is called a* ***valuation operator.*** □

## 6.3 Riesz's Theorem

Using our terminology all valuation operators are linear functionals of the form $\mathcal{L} : V \to \mathbb{R}$ for some vectorspace $V$, so we can apply the following theorem of Frigyes Riesz which (and all the other results cited in the subsequent Sections) can be found in any linear algebraic book.

**Theorem 6.3** *(Representation Theorem of F. Riesz) If* $V$ *is any finite dimensional linear space with an arbitrary scalar product* $< ., . >: V \times V \to \mathbb{R}$ *then for every linear functional* $\mathcal{L} : V \to \mathbb{R}$ *there is a (unique) fixed vector* $\underline{a} \in V$ *(depending only on* $\mathcal{L}$*) such that*

$$\mathcal{L}(\underline{v}) =< \underline{a}, \underline{v} > \tag{6.1}$$

*holds for every vector* $v \in V$ . □

Since Riesz's theorem is valid for *any* scalar product $<, >$ (symmetric, positive definite and bilinear function from $V \times V$ to $\mathbb{R}$) on the space $V$, for applications we may choose first the Euclidean product

$$< \underline{u}, \underline{v} >:= \sum_{i=1}^{n} u_i v_i$$

where $[u_1, \ldots, u_n]^T$ and $[v_1, \ldots, v_n]^T$ denote the coordinates of $\underline{u}$ and $\underline{v}$ with respect to a *fixed* base $B \subseteq V$ . (We discuss all the possible scalar products of $\mathbb{R}^n$ and the connections among them in Section 6.5.)

So we get the following special case of Riesz's Theorem:

**Theorem 6.4** *If $V$ is any finite dimensional linear space with any fixed base $\{\underline{b}_1, \ldots, \underline{b}_n\} \subseteq V$ then for every linear functional $\mathcal{L} : V \to \mathbb{R}$ there is a (unique) fixed vector $\underline{\mathbf{a}} \in V$ (depending only on $\mathcal{L}$) such that*

$$\mathcal{L}(\underline{v}) = \sum_{i=1}^{n} a_i v_i \tag{6.2}$$

*holds for every vector $v \in V$ where $[a_1, \ldots, a_n]$ and $[v_1, \ldots, v_n]$ denote the co-ordinates of $\underline{\mathbf{a}}$ and $\underline{v}$ with respect to the base $B$ .* □

Using (6.2) this latter variant of Riesz's Theorem tells us for valuation operators (e.g. in our examples above) the following:

**Corollary 6.5** *If the linear space $\mathbb{R}^N$ is determined by the components $\{C_1, \ldots, C_N\}$ , then for any valuation operator $\mathcal{L} : \mathbb{R}^N \to \mathbb{R}$ there is a unique vector $\underline{a} = [a_1, \ldots, a_N]^T \in \mathbb{R}^N$ such that $\mathcal{L}$ can be computed as*

$$\mathcal{L}(S) = \sum_{i=1}^{N} a_i \cdot s_i \tag{6.3}$$

*for any structure $S = \sum_{i=1}^{N} s_i \cdot C_i$ .* □

(Recall Definition 6.1 for the notion of components and structures.)

This clearly means that the values of *every* valuation operator on *any* structures in *all of the examples:* not only is determined by the components involved but simply it is *the weighted sum of the numbers of the components in the structure.*

This observation might facilitate the investigations of any valuation operators in any of our (or other) examples. For example, we have to determine only the coefficient vector $\underline{a} \in \mathbb{R}^N$ for the given valuation operator and after this we can trivially count (or further investigate) its value on the basis of (6.3).

The above result might be not new for chemists: trivially the linearity of $\mathcal{L}$ implies

$$\mathcal{L}(S) = \mathcal{L}\left(\sum_{i=1}^{N} s_i \cdot C_i\right) = \sum_{i=1}^{N} s_i \cdot \mathcal{L}(C_i) \tag{6.4}$$

which clearly implies (6.3) choosing $a_i := \mathcal{L}(C_i)$ for $i = 1, \ldots, N$. Let us remark here that the above computation assumes that $\mathcal{L}$ can be computed for components $C_i$ on the same way as for structures $\underline{S}$ .

However, the real power of Riesz' Theorem lies in the fact that it is valid for *any* scalar product on *any* linear space $V$. We used it only in the very special case of Euclidean scalar product *with respect to* the base $\{C_1, \ldots, C_n\}$ of our interested components! The variety of and the connections among different scalar products and bases in $\mathbb{R}^n$ is explained in Section 6.5.

One surprising application of the above results is a one-sentence proof of Hess' law in thermochemistry.

**Theorem 6.6** *(**Hess' law**) If a linear combination of the reactions $X_1, \ldots, X_k$ results the zero (i.e. void) mechanism $\underline{\mathcal{M}}$ then the sum (the same linear combination) of the reaction heats $\mathcal{H}(X_j)$ of the reactions $X_j$ will also be 0.*

**Proof.** This is trivial since if $\sum_{j=1}^{k} \lambda_j X_j = \underline{\mathcal{M}}$ then

$$\mathcal{H}\left(\sum_{j=1}^{k} \lambda_j X_j\right) = \mathcal{H}(\underline{\mathcal{M}}) = 0 \ . \tag{6.5}$$

■

The following theorem is also well known, using it we can give bounds for the values of $\mathcal{L}(S)$ in advance:

**Theorem 6.7** *(Cauchy -Bunyakowsky-Schwarz) For any linear space $V$ and scalar product $<,>: V \times V \to \mathbb{R}$ on $V$ the equality*

$$|\langle \underline{a}, \underline{x} \rangle| \leq \|\underline{a}\| \cdot \|\underline{x}\| \tag{6.6}$$

*holds for every vectors $\underline{a}, \underline{x} \in V$ where $\|\underline{x}\| := \sqrt{< \underline{x}, \underline{x} >}$ is the norm of all the vectors $\underline{x} \in V$ .* □

**Corollary 6.8** *For any linear space $V$ with the arbitrary scalar product $<,>: V \times V \to \mathbb{R}$ on it and for any linear functional $\mathcal{L} : V \to \mathbb{R}$ we have*

$$\mid \mathcal{L}(\underline{S}) \mid \leq c \cdot \|\underline{S}\| \tag{6.7}$$

*for any vector $S \in V$ where $c \in \mathbb{R}$ is a fixed constant depending on $\mathcal{L}$ and on the scalar product $<,>$ only (but not the vector $\underline{S}$ itself).* □

Using (6.7) we can estimate the magnitude of $\mathcal{L}(S)$. For example, if $<,>$ is the Euclidean (quadratic) scalar product on $\mathbb{R}^N$ then we have

$$\mid \mathcal{L}(S) \mid \leq c \cdot \sqrt{s^2 + \ldots + s_N^2} \tag{6.8}$$

where

$$c = \sqrt{a^2 + \ldots + a^2}$$

(the quadratic sum of the $\mathcal{L}$-values of the componets) and $\underline{a}$ is defined in (6.2) in Theorem 6.4.

## 6.4 Direct sums

In all of the above results we had to fix the dimension of the space in advance. This clearly fixes the number of components which can be used.

In this Section we explain the possibility of later (subsequent) adding new structures containing new components, i.e. how to extend the dimension of the space we are in, and continue the calculations without giving up the old ones. Though the below results solve this problem we must be careful in practical computations.

Extending the dimension by introducing new base vectors (components in our examples) can be handled with *direct sums* of linear spaces and of linear operators.

Let us recall here that the **direct sum** $V = V_1 \oplus V_2$ means that *each* vector $\underline{v} \in V$ can be written *uniquely* in the form $\underline{v} = \underline{v}_1 + \underline{v}_2$ for some $\underline{v}_1 \in V_1$ and $\underline{v}_2 \in V_2$ (which clearly implies $V_1 \cap V_2 = \{0\}$). Further, $\mathcal{L} := \mathcal{L}_1 \oplus \mathcal{L}_2$ means $\mathcal{L}(\underline{v}) = \mathcal{L}_1(\underline{v}_1) + \mathcal{L}_2(\underline{v}_2)$ for the linear operators $\mathcal{L} : V \to \mathbb{R}$, $\mathcal{L}_1 : V_1 \to \mathbb{R}$, $\mathcal{L}_2 : V_2 \to \mathbb{R}$ and for any vectors $\underline{v}$, $\underline{v}_1$, $\underline{v}_2$ above.

**Theorem 6.9** *If $V$ is any linear space which is a direct sum of the two spaces $V = V_1 \oplus V_2$ then every linear functional $\mathcal{L} : V \to \mathbb{R}$ can be written in the form $\mathcal{L} = \mathcal{L}_1 \oplus \mathcal{L}_2$ where $\mathcal{L}_i : V_i \to \mathbb{R}$ are linear functionals for $i = 1, 2$.*

*On the other hand, if $\mathcal{L}_i : V_i \to \mathbb{R}$ are linear functionals for $i = 1, 2$ then the function $\mathcal{L} := \mathcal{L}_1 \oplus \mathcal{L}_2$ , $\mathcal{L} : V \to \mathbb{R}$ is also linear.* $\square$

Using Riesz' Theorem 6.3 for all the vector spaces $V$, $V_1$ and $V_2$ separately, clearly we have that $\mathcal{L}(\underline{v}) =< \underline{a}, \underline{v} >$, $\mathcal{L}_1(\underline{v}_1) =< \underline{a}_1, \underline{v}_1 >$ and $\mathcal{L}_2(\underline{v}_2) = < \underline{a}_2, \underline{v}_2 >$ hold for all vectors $\underline{v} \in V$, $\underline{v}_1 \in V_1$ and $\underline{v}_2 \in V_2$ for some fixed special vectors $\underline{a} \in V$, $\underline{a}_1 \in V_1$ and $\underline{a}_2 \in V_2$ . Let us emphasize however that $\underline{a}$ is *not* the (direct) sum of $\underline{a}_1$ and $\underline{a}_2$ in general. This latter requirement can be ensured e.g. when the subspaces $V_1$ and $V_2$ are *orthogonal* to each other (with respect to the scalar product $<,>$) which means $\underline{v}_1 \perp \underline{v}_2$ (i.e. $< \underline{v}_1, \underline{v}_2 >= 0$) for *all* $\underline{v}_1 \in V_1$, $\underline{v}_2 \in V_2$ . We state the exact result below.

**Theorem 6.10** *If $V = V_1 \oplus V_2$ and $\mathcal{L} = \mathcal{L}_1 \oplus \mathcal{L}_2$ are arbitrary as in Theorem 6.9, $<,>: V \times V \to \mathbb{R}$ is an arbitrary scalar product such that $V_1$ and $V_2$ are orthogonal to each other (with respect to this scalar product) and further the vectors $\underline{a} \in V$, $\underline{a}_1 \in V_1$ and $\underline{a}_2 \in V_2$ satisfy*

$$\mathcal{L}(\underline{\mathbf{v}}) =< \underline{a}, \underline{v} >,\ \mathcal{L}_1(\underline{v}_1) =< \underline{a}_1, \underline{v}_1 > \text{ and } \mathcal{L}_2(\underline{v}_2) =< a_2, \underline{v}_2 >$$

*for all $\underline{v} \in V$, $\underline{v}_1 \in V_1$ and $\underline{v}_2 \in V_2$ , then*

$$\underline{a} = \underline{a}_1 \oplus \underline{a}_2 = \underline{a}_1 + \underline{a}_2 \ . \quad \square \tag{6.9}$$

In order to formulate extensions of valuation operators we need the concept and the notation of **restriction**

$$\mathcal{L} \mid_H : H \to W$$

of any linear mapping $\mathcal{L} : V \to W$ and subspace $H$ of $V$ (in our applications $V = \mathbb{R}^N$ and $W = \mathbb{R}$).

Clearly

$$\mathcal{L} = \mathcal{L} \mid_{V_1} \oplus \mathcal{L} \mid_{V_2}$$

holds for any linear mapping $\mathcal{L} : V \to W$ and subspaces $V_1$, $V_2$ of $V$ if $V = V_1 \oplus V_2$ .

**Corollary 6.11** *If the vectors* $\underline{a} \in \mathbb{R}^N$, $\underline{b} \in \mathbb{R}^M$ *are determined by the arbitrary but disjoint sets of components* $\{C_1, \ldots, C_N\}$ *and* $\{D_1, \ldots, D_M\}$ *and by the (arbitrary) valuation operators* $\mathcal{L}_1 : \mathbb{R}^N \to \mathbb{R}$, $\mathcal{L}_2 : \mathbb{R}^M \to \mathbb{R}$ , *which are restrictions of the same valuation operator* $\mathcal{L} : \mathbb{R}^{N+M} \to \mathbb{R}$ , *then*

$$\mathcal{L}(S) = \sum_{i=1}^{N} a_i \cdot s_i + \sum_{j=1}^{M} b_j \cdot s_{N+j} \tag{6.10}$$

*holds for any structure* $S = \sum_{i=1}^{N+M} s_i \cdot C_i \in \mathbb{R}^{N+M}$ . $\square$

The above result allows us just to add the values of $\mathcal{L}(S_1)$ and $\mathcal{L}(S_2)$ to get the value of $\mathcal{L}(S)$ if $S = S_1 + S_2$ is *any* but disjoint partitioning (concerning the involved components) of the structure $S$. In other words, applying newer components (either atoms or species or reactions, etc.) we are allowed just only to extend our previous databases, the *linearity* of $\mathcal{L}$ ensures that *no* new data or computational methods are neccessary.

## 6.5 Scalar products

We give here a brief summary of scalar products in any finite dimensional linear space, revealing both the variety and boundary of them and also the connections among them. This helps us to find the exact role of the Eucledian scalar product we used in Section 6.1 for a fixed base of the space. All notions and results can be found in any standard graduate level linear algebraic textbook.

First we have to to clarify some notions.

**Definition 6.12** *The matrix* $\mathbf{A} \in \mathbb{R}^{nxn}$ *is* ***symmetric*** *if* $\mathbf{A}^T = \mathbf{A}$ *, in other words* $a_{i,j} = a_{j,i}$ *for* $i, j = 1, \ldots, n$ *where* $a_{i,j}$ *are the entries of* $\mathbf{A}$ *.*

*For* $i \leq n$ *the* ***i-th main subdeterminant*** *or* ***main minor*** $\mathbf{d_i} \in \mathbb{R}$ *of* $\mathbf{A}$ *is the determinant of the left-upper submatrix of size* $i \times i$ *of* $\mathbf{A}$ *formed by the first* $i$ *many rows and columns of* $\mathbf{A}$ *.*

*The matrix is* ***positive definite*** *iff all its main minors* $d_1, \ldots, d_n$ *are positive.* $\square$

In what follows let $V$ be any fixed finite dimensional linear space of dimension $n \in \mathbf{N}$ with any fixed base $B = \{b_1, \ldots, b_n\} \subseteq V$ . (No special role at all will possess the base we chose in what follows.) In what follows, we will not force any distinction of the vectors $\underline{u} \in V$ and their co-ordinates $[u_1, \ldots, u_n]^T \in \mathbb{R}^n$ with respect to the fixed base $B$.

**Theorem 6.13** *The mapping* $\mathcal{A} : V \times V \to \mathbb{R}$ *,*

$$\mathcal{A}(\underline{u}, \underline{v}) := \underline{u}^T \mathbf{A} \underline{v} = \sum_{i=1}^{n} \sum_{,j=1}^{n} a_{i,j} \cdot u_i \cdot v_j$$

*is bilinear for any matrix* $\mathbf{A} \in \mathbb{R}^{n \times n}$*.* $\mathcal{A}$ *is symmetric if and only if* $\mathbf{A}$ *is symmetric.* $\mathcal{A}$ *is positive definite (i.e.* $\mathcal{A}(\underline{u}, \underline{u}) > 0$ *for* $\underline{u} \in V$*,* $\underline{u} \neq \underline{0}$*) if and only if* $\mathbf{A}$ *is positive definite.* $\square$

The below two results together give a complete characterization of scalar products on any finite dimensional vectorspace.

**Corollary 6.14** *The mapping* $\mathcal{A} : V \times V \to \mathbb{R}$ *,*

$$\mathcal{A}(\underline{u}, \underline{v}) := \underline{u}^T \mathbf{A} \underline{v}$$

*is always a scalar product on* $V$ *for any symmetric and positive definite matrix* $\mathbf{A} \in \mathbb{R}^{nxn}$ *.* $\square$

**Theorem 6.15** *For any scalar product* $\mathcal{A} : V \times V \to \mathbb{R}$ *there is a (unique) matrix* $\mathbf{A} \in \mathbb{R}^{nxn}$ *such that* $\mathcal{A}(\underline{u}, \underline{v}) = \underline{u}^T \mathbf{A} \underline{v}$ *.* $\square$

$\mathbf{A}$ clearly depends on the base $B \subseteq V$ of the space but there are simple formulae for transforming the above matrices of a fixed scalar product $\mathcal{A}$ to *any* other base. Even special bases can easily been found by the below result.

**Theorem 6.16** *(Gram–Schmidt) For any scalar product $\mathcal{A} : V \times V \to \mathbb{R}$ in any finite dimensional linear space $V$ there is a base $F = \{\underline{f}_1, \dots, \underline{f}_n\} \subseteq V$ in which elements are orthogonal with respect to $\mathcal{A}$, i.e. $\mathcal{A}(\underline{f}_i, \underline{f}_j) = 0$ for $i \neq j$ .* □

**Corollary 6.17** *If $\mathcal{A}$ and $F$ are as in the above theorem then the matrix $\mathbf{A}$ , corresponding to $\mathcal{A}$ and $F$ , is diagonal with positive entries, that is for every $\underline{u}, \underline{v} \in V$ we have*

$$\mathcal{A}(\underline{u}, \underline{v}) = \underline{u}^T A \underline{v} = \sum_{i=1}^{n} a_{i,i} u_i v_i$$

*where the coefficients $a_{i,i} \in \mathbb{R}$ are all positive.* □

The next (and last) result summarizes the connections among different *scalar products* on a given finite dimensional linear space: *there is* no *difference at all among different scalar products on a fixed linear space $V$ – from the topological point of view, at least.*

**Theorem 6.18** *For any two scalar products $\mathcal{A}, \mathcal{B} : V \times V \to \mathbb{R}$ there is an automorphism $\mathcal{I} : V \to V$ such that*

$$\mathcal{A}(\underline{u}, \underline{v}) = \mathcal{B}(\mathcal{I}(\underline{u}), \mathcal{I}(\underline{v}))$$

*holds for any vectors $\underline{u}, \underline{v} \in V$. Moreover, $\mathcal{I}$ is continuous with respect to the topologies induced by $\mathcal{A}$ and $\mathcal{B}$, i.e. $\mathcal{I} : (V, \mathcal{A}) \to (V, \mathcal{B})$ is a (topological) homeomorphism.* □

Our first application of the above result is to the Euclidean scalar product, of course. This last Theorem says especially, among others that any valuation operator can be measured in any measure unit, up to a scalar factor.

# Chapter 7

# Beyond the thesis

During our theoretical investigations on the topic of the present Thesis (mainly mathematical we mean) a dozen of further questions arose. In this Chapter we shortly list these ideas for further investigations.

## 7.1 On the algorithm

We mentioned in Chapter 3 "*The algorithm*" Mr. Bertók's graph theoretical algorithm. Because of the close connections between our algorithms, it would be fruitful to synthesize both of our ideas.

**Problem 7.1** *Study the connections between graph theoretical and linear algebraic methods.* □

For example, one can extract data from *p-graphs* for PNS (*Process Network Syntheses*) to feed our linear algebraic algorithm, a simple example is given in Figure on the next page.

*First* we suspect that additional information, included in the graph, can be coded among the input vectors (similar to that we suceeded in Section 3.2 several time, or order of the reactions, requiring one another, etc.), and *second*, we can synthesize the linear algebraic and graph theoretical methods. These results are planned to summarize in [$Sz01a$] and [$Sz01b$] .

## 7.2 More exact lower bounds

We also have mentioned the question of minimal number of simplexes in higher dimensions if *no parallel* vectors are allowed among the vectors.

**Conjecture 7.2** *Suppose that $\mathcal{H}$ is of fixed size, spans $\mathbb{R}^n$ and contains **no** collinear vectors. Then the minimal value of $simp(\mathcal{H})$ is is attained precisely in the following configurations:*

***1.*** *If $n$ is even, $\mathcal{H}$ contains $n$ linearly independent vectors $\{u_i : i = 1, \dots, n\}$ and the remaining ones are divided as evenly as possible between the planes $\{[u_i, u_{i+1}] : i = 1, 3, \dots, n-1\}$.*

***2.*** *If $n$ is odd, $\mathcal{H}$ again contains $n$ linearly independent vectors $\{u_i : i = 1, \dots, n\}$, one extra vector in the plane $[u_{n-1}, u_n]$ and finally the remaining vectors divided as evenly as possible between the planes $\{[u_i, u_{i+1}] : i = 1, 3, \dots, n-2\}$ with lower indices having precedence.* □

Similar questions (with similar methods) can be raised also for matroids, see $[SzDHL01]$. In more general, one could ask the following:

**Problem 7.3** *" What is the minimal number of simplexes if assuming the minimal size of dependent subsets ('circles' in matroids) is at least $k$ for any fixed $k \in \mathbb{N}$ ?* □

(The minimal size of dependent subsets is called the **girth** of the matroid.) With prof. Oxley together we have conjectures concerning this question we are working on. One of our conjectures is the following.

**Conjecture 7.4** *For matroids $\mathcal{M}$ of size $m$ and with rank $k$ , minimal number of circuits is contained in the uniform matroid $U_{k,n-3}$ , so the lower bound is*

$$1 + 3 \cdot \binom{m-3}{k-1} + 3 \cdot \binom{m-3}{k-2} + \binom{m-3}{k-3} \leq simp(\mathcal{M}) \quad . \qquad \square$$

Some related questions will be included in our joint work $[SzDHL01]$ .

Another variant on the number of simplexes is when we have to count simplexes containing one fixed reaction $S_R$ of the given ones, or the simplexes which contain *at least one* vector from the set $\{V_1, \dots, V_t\}$ . More precisely we ask:

**Problem 7.5** *Let the set of vectors $\mathcal{H} := \{A_1, ..., A_m\} \subset \mathbb{R}^N$ and a subset*

$$\mathcal{V} := \{V_1, \dots, V_t\} \subset \mathcal{H}$$

*of $\mathcal{H}$ be given. What is the possible minimal and maximal number of simplexes $\mathcal{S} \subset \mathcal{H}$ containing at least one vector from the set $\mathcal{V}$ , that is*

$$\mathcal{S} \cap \mathcal{V} \neq \emptyset \qquad ? \qquad \square$$

This bound would be important for the bound for the running time of our modified algorithm, see Sections 3.2 and the Appendix "*Computational results*".

## 7.3 Hierarchies

We have already observed the general linear algebraic study of *hierarchies* among atoms- species- reactions- mechanisms- etc., this concept will be discussed in general in [$SzP01$] . Here we introduce the idea of hierarchies. Roughly speaking, our idea is as follows.

**Definition 7.6** *Let the vectors of the i 'th hierarchy ($i \in \mathbb{N}$) be*

$$H_i := \{A_1^{(i)}, ..., A_{k_i}^{(i)}\} \subset \mathbb{R}^{n_i} \quad .$$

*Suppose, that the set of simplexes of $H_i$ is*

$$\mathcal{S}_i := \{S_1^{(i)}, ..., S_{t_i}^{(i)}\} \subseteq \mathcal{P}(H_i)$$

*and identify these simplexes to the set of indices*

$$S_j^i := \{u \leq k_i : A_u \in S_j^i\} \quad \subseteq \{1, ..., k_i\} \ , \quad (j \leq t_i) \quad .$$

*Suppose further that these simplexes determine (up to a constant factor) the linear combinations*

$$\sum_{v \in S_j^i} \lambda_v^{i,j} A_v = \underline{0} \qquad (j \leq t_i).$$

*Then we define the vectors of the* ***next hierarchy*** *as*

$$A_j^{(i+1)} := [\mu_1, ..., \mu_{k_i}] \quad \in \mathbb{R}^{k_i} \ , \quad (j \leq t_i) \ ,$$

*where*

$$\mu_v = \begin{cases} \lambda_v^{i,j} & \text{if } v \in S_j^i \\ 0 & \text{if } v \notin S_j^i \end{cases} \ ,$$

*so, of course, the next dimension is*

$$n_{i+1} = k_i \quad . \qquad \square$$

Then we propose the next problem:

**Problem 7.7** *Study the properties of this hierarchy, the connections among these levels, and study their applications to linear algebra, chemistry, physics, etc.* $\square$

Professor Peter H.Sellers was kind as to share his general ideas for further research in [$S02$] which are extremaly useful for the present problem.

## 7.4 Theoretical questions

In [$Sz01a$] we plan to discuss in full detail the effect of extending the dimension of the vectors we proposed because of the law of mass balance (preservation of material) explained in Subsection 3.2.1 in Chapter 3.

**Problem 7.8** *Discuss the theoretical and algorithmic effects of extending the dimension of the vectors we proposed in Subsection 3.2.1 in Chapter 3.* □

This problem is related to Problem 7.1 above, since in both cases we extended either the dimension or the number of vectors, or both.

These modifications, of course have effect to the running time of the algorithm, which is always contained in our investigations.

After a clear linear algebraic reformulation we plan to deal with the question, based on Professor Árpád Pethő's fundamental work [$P67$] , and this is also a central question in researches of Happel-Sellers-Otarod [$HS83$] , [$HOS90$] and Friedler-Fan-Bertók [$FBF00$] and [$B99$] :

**Problem 7.9** *"Is there a (finite) set of mechanism/reactions which linear combinations would give the set of all mechanism/reactions"*
*Find this set theoretically, algorithmically, and/or describe its properties.* □

Convex linear combinations clearly are not sufficient as it is wellknown from linear algebra.

# Chapter 8

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# Computational results

In this Chapter we present some concrete computational results for illustrating the output and the *speed* of our algorithm and the effect of its variations described in Chapter 3. "*The algorithm and its variations*".

As we discussed in Chapter 3, the algorithm requires *polynomial* time in the size of the input (the number of vectors) in fixed dimension. According to this estimation, everyday size inputs (some dozens of vectors in 10-20 dimensional spaces) require some seconds only on modern computers, but we can get answer in the case of hundreds of vectors in similar dimensions in some hours, too.

Concrete computational experiments on (also large) datasets are shown in the present Chapter. We used Borland's Turbo Pascal 6.0 language and a Packard-Bell PC with Pentium II. processor of 360 MHz.

The computing results of Happel-Otarod-Sellers[$HOS90$] and Bertók [$B99$] require also about this running time but their results are not better at all than of ours.

When a so called "resulting" (overall) reaction $S_R$ is given (which we have build from a linear combination of the other vectors) we made run our program in two ways: we computed *all* simplexes (not regarding the extra role of $S_R$) and we also computed the mechanisms resulting the (overall) reaction $S_R$ (i.e.the simplexes *only* which contain $S_R$, see the subsection 3.2.1). Checking this latter requirement in each step slowed down slightly our computer but our formula

$$\nu(VarAll) = \nu(VarOnly) + \nu(VarOrig)$$

as (3.5) in subection 3.2.1 from Chapter 3 "*The algorithm and its variations*" is justified now.

# .1 Amundson

Our first example is taken from **Amundson** [*A*66] and also can be found in [*P*90]. We have given the groups of atoms (functional bonds) $CO$, $CO_2$, $O_2$, $H_2$, $CH_2O$, $CH_3OH$, $C_2H_5OH$, $(CH_3)_2CO$, $CH_4$, $CH_3CHO$, $H_2O$ (of course there is *no* resulting (overall) reaction now). The 213 minimal reactions (simplexes) we also get by our computation, are listed in detail eg.in [*P*90]. Since we use three atoms $C, O, H$ (i.e. the input consists of 3- dimensional vectors) and there are no parallel vectors among the species we can use the sharper lower bound from Corollary 4.10 from Chapter 4 "*On the number of simplexes*".

| | |
|---|---|
| $N$ (dimension of the vectorspace) | 3 |
| $n$ (dimension of what $H$ spans) | 3 |
| $M$ (number of input vectors: $\|H\|$) | 11 |
| $simp(H)$ (number of simplexes) | 213 |
| $1 + \binom{M-2}{3} + \binom{M-3}{2}$ (lower bound) | $113 \leq$ |
| $\binom{M}{n+1}$ (upper bound) | $\leq 330$ |
| $t$ (computational time [sec]) | $0.22s$ |
| number of checked subsets of $H$ | 502 |

*"Amundson"*
**Table 8.1**

# .2 Ammonia

Our next example is called **"Ammonia"** in [*HOS*90] and it is the 4'th example in [*B*99]. The resulting (overall) and the examined (*"possible elementary"*) reactions are:

$\mathbf{S}_R$: $\mathbf{N_2}+\mathbf{3H_2}\rightarrow \mathbf{2NH_3}$
$S_1 : N_2 + \ell = N_2\ell$
$S_2 : N_2\ell + H_2 = N_2H_2\ell$
$S_3 : N_2H_2\ell + \ell = 2NH\ell$
$S_4 : N_2 + 2\ell = 2N\ell$
$S_5 : N\ell + H\ell = NH\ell + \ell$
$S_6 : NH\ell + H\ell = NH_2\ell + \ell$
$S_7 : NH\ell + H_2 = NH_3 + \ell$
$S_8 : H_2 + 2\ell = 2H\ell$
$S_9 : NH_2\ell + H\ell = NH_3 + 2\ell$

where $\ell$ denotes the catalysator's surface.

After running our algorithm we get the following minimal mechanisms:

1) $3S_1 + 3S_2 + 3S_3 - 2S_4 - 4S_5 + 2S_6 + 2S_9 = S_R$
2) $S_1 + S_2 + S_3 + 2S_6 + 2S_8 + 2S_9 = S_R$
3) $S_1 + S_2 + S_3 + 2S_7 = S_R$
4) $S_4 + 2S_5 - S_6 + 3S_7 - S_9 = S_R$
5) $S_4 + 2S_5 + 2S_6 + 3S_8 + 2S_9 = S_R$
6) $S_4 + 2S_5 + 2S_7 + S_8 = S_R$
7) $-S_1 - S_2 - S_3 + S_4 + 2S_5 - S_6 + S_7 - S_9 = 0$
8) $S_1 + S_2 + S_3 - S_4 - 2S_5 - S_8 = 0$
9) $-S_6 + S_7 - S_8 - S_9 = 0$

(The latter three mechanisms yield not $S_R$ but the zerovector - a cycle.)

| | Total | Containing $S_R$ only |
|---|---|---|
| $N$ (dimension of the vectorspace) | 10 | 10 |
| $n$ (dimension of what $H$ spans) | 7 | 7 |
| $M$ (number of input vectors: $\|H\|$) | 10 | 10 |
| $simp(H)$ (number of simplexes) | 9 | 6 |
| $b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound) | $3 \leq$ | $1 \leq$ |
| $\binom{M}{n+1}$ (upper bound) | $\leq 45$ | $\leq 36$ |
| $t$ (computational time [sec]) | $0.44s$ | $0.28s$ |
| number of checked subsets of $H$ | 969 | 473 |

*"Ammonia"*
**Table 8.2**

# .3 Bertók_5

Our next example is **Bertók's 5'th** example from [$B99$] which is taken from [$HS83$]. The resulting (overall) and the examined (*possible elementary*) reactions are:

$\mathbf{S}_R$: $\mathbf{2H_2{+}2CO \rightarrow CH_4{+}CO_2}$
$S_1 : CO\ell + \ell = C\ell + O\ell$
$S_2 : C\ell + H\ell = CH\ell + \ell$
$S_3 : CH\ell + H\ell = CH_2\ell + \ell$
$S_4 : CH_2\ell + H\ell = CH_3\ell + \ell$
$S_5 : CH_3\ell + H\ell = CH_4 + 2\ell$
$S_6 : OH\ell + H\ell = H_2O + 2\ell$
$S_7 : CO_2 + \ell = CO_2\ell$
$S_8 : CO + \ell = CO\ell$
$S_9 : H_2 + 2\ell = 2H\ell$
$S_{10} : CO_2\ell + H\ell = CHOO\ell + \ell$
$S_{11} : CHOO\ell + H\ell = CHO\ell + OH\ell$
$S_{12} : O\ell + H\ell = OH\ell + \ell$
$S_{13} : CO\ell + O\ell = CO_2\ell + \ell$
$S_{14} : CHOO\ell + \ell = OH\ell + CO\ell$
$S_{15} : CO\ell + H\ell = CHO\ell + \ell$

Now all the minimal mechanisms (the output) are:

1) $S_1 + S_2 + S_3 + S_4 + S_5 - S_7 + 2S_8 + 2S_9 - S_{10} - S_{11} + S_{12} + S_{15} = S_R$
2) $S_1 + S_2 + S_3 + S_4 + S_5 - S_7 + 2S_8 + 2S_9 - S_{10} + S_{12} - S_{14} = S_R$
3) $S_1 + S_2 + S_3 + S_4 + S_5 - S_7 + 2S_8 + 2S_9 + S_{13} = S_R$
4) $S_{10} + S_{11} - S_{12} + S_{13} - S_{15} = 0$
5) $S_{10} - S_{12} + S_{13} + S_{14} = 0$
6) $S_{11} - S_{14} - S_{15} = 0$

| | Total | Containing $S_R$ only |
|---|---|---|
| $N$ (dimension of the vectorspace) | 17 | 17 |
| $n$ (dimension of what $H$ spans) | 13 | 13 |
| $M$ (number of input vectors: $\|H\|$) | 16 | 16 |
| $simp(H)$ (number of simplexes) | 6 | 3 |
| $b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound) | $4 \leq$ | $1 \leq$ |
| $\binom{M}{n+1}$ (upper bound) | $\leq 120$ | $\leq 105$ |
| $t$ (computational time [sec]) | $78.60s$ | $43.28s$ |
| number of checked subsets of $H$ | $63,429$ | $31,697$ |

*"Bertók_5"*
**Table 8.3**

# .4 Bertók_rn.in

This example was provided for us by Mr.Bertók personally as **_rn.in** and was presented in [$FBF00$]. The resulting (overall) and the examined (*possible elementary)* reactions now are ($S_{22}$ is omitted by technical purposes):

$S_R : N_2 + 3H_2 = 2NH_3$

$S_1 : H_2 + \ell = H_2\ell$
$S_2 : H_2\ell + \ell = 2H\ell$
$S_3 : N_2 + \ell = N_2\ell$
$S_4 : N_2\ell + \ell = 2N\ell$
$S_5 : N_2\ell + H_2\ell = N_2H_2\ell + \ell$
$S_6 : N_2H_2\ell + \ell = NH\ell + NH\ell$
$S_7 : N\ell + H\ell = NH\ell + \ell$
$S_8 : NH\ell + H\ell = NH_2\ell + \ell$
$S_9 : NH\ell + H_2\ell = NH_3\ell + \ell$
$S_{10} : NH\ell + N\ell = N_2H\ell + \ell$
$S_{11} : NH_2\ell + H\ell = NH_3\ell + \ell$
$S_{12} : NH_2\ell + N\ell = N_2H_2\ell + \ell$
$S_{13} : N_2H_2\ell + H_2\ell = N_2H_4\ell + \ell$
$S_{14} : N_2H_2\ell + N_2\ell = N_4H_2\ell + \ell$
$S_{15} : N_2H_4\ell + H\ell = NH_2\ell + NH_3\ell$
$S_{16} : N_2H_4\ell + N\ell = N_2H\ell + NH_3\ell$
$S_{17} : H\ell + N_2\ell = N_2H\ell + \ell$
$S_{18} : N\ell + H_2\ell = NH\ell + H\ell$
$S_{19} : H\ell + N_2\ell = NH\ell + N\ell$
$S_{20} : H\ell + N_2H_2\ell = NH_2\ell + NH\ell$
$S_{21} : N\ell + N_2H_2\ell = N_2H\ell + NH\ell$
$S_{23} : H\ell + N_2H\ell = NH\ell + NH\ell$
$S_{24} : H\ell + N_2H\ell = NH_2\ell + N\ell$
$S_{25} : NH_3\ell = NH_3 + \ell$

Our calculations are summarized in the below Table:

| | Total | Containing $S_R$ only |
|---|---|---|
| $N$ (dimension of the vectorspace) | 15 | 15 |
| $n$ (dimension of what $H$ spans) | 14 | 14 |
| $M$ (number of input vectors: $\|H\|$) | 25 | 25 |
| $simp(H)$ (number of simplexes) | 5,609 | 3,585 |
| $b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound) | $11 \leq$ | $1 \leq$ |
| $\binom{M}{n+1}$ (upper bound) | $\leq 3,268,760$ | $\leq 1,961,256$ |
| $t$ (computational time [sec]) | $2.1 \cdot 10^4 s$ $\approx 5h50\,\text{min}$ | $1.2 \cdot 10^4 s$ $\approx 3h21\,\text{min}$ |
| number of checked subsets of $H$ | 10,664,430 | 2,846,629 |

*"Bertók_rn.in"*
**Table 8.4**

Let us mention that Bertók achieved the same list of simplexes as ours but in 13 hours computer run comparing to our 3 hours 21 minutes.

The following three examples illustrates the modifications described in Section 3.2.

## .5 Ethylene Oxide

This example is introduced in[$HOS90$] as **Ethylene Oxide Synthesis.** We are given the following reactions

$S_1$ : $O_2 + \ell = O_2\ell$
$S_2$ : $2O\ell = O_2\ell + \ell$
$S_3$ : $O_2\ell + C_2H_4 = O\ell + CH_3CHO$
$S_4$ : $C_2H_4O + \ell = C_2H_4O\ell$
$S_5$ : $O_2\ell + C_2H_4 = C_2H_4O + O\ell$
$S_6$ : $5O_2\ell + CH_3CHO = 5O\ell + 2CO_2 + 2H_2O$
$S_7$ : $C_2H_4O\ell = O\ell + C_2H_4$

where the terminal (chemical) species are $C_2H_4O$, $C_2H_4$, $O_2$, $CO_2$ and $H_2O$, all the others are intermediate (active) ones.

As we indicated at the end of Section 3.2 we can find all (possible) direct overall reactions among the above set of terminal species by our algorithm (as detailed in Section 3.2). We got the following (complete) list of minimal reactions

$d_1$) $1C_2H_4 + {}^1/_2O_2 - C_2H_4O = 0$
$d_2$) ${}^1/_2C_2H_4 + {}^3/_2O_2 - CO_2 - H_2O = 0$
$d_3$) ${}^5/_2C_2H_4 + 3C_2H_4O - CO_2 - H_2O = 0$
$d_4$) ${}^5/_4O_2 + {}^1/_2C_2H_4O - CO_2 - H_2O = 0$

in 0.00 sec which corresponds (in order) to $d_1, d_3, d_4, d_2$ of [$HOS90$], respectively. Computational data concerning this run are shown in the first column of Table 8.5.

The second column of this table shows searching for mechanisms (resulting the zero vector, i.e. the void reaction) among the original vectors (reactions $S_1$ through $S_7$). The single mechanisms we found shows that the reactions $S_1, \ldots, S_7$ are *not* linearly independent.

Columns 3 and 4 show computation when we introduced the new vectors $V_1, \ldots, V_5$ representing one-to-one the terminal (chemical) species as we suggested in the first part of Section 3.2. For comparison of CPU time we run the algorithm first for *all* simplexes then for those which contain at least one new vector $V_i$ only.

We have the following list of minimal mechanisms:

$m_1$ : ${}^7/_6C_2H_4 + O_2 - C_2H_4O - {}^1/_3CO_2 - {}^1/_3H_2O + S_1 + {}^1/_6S_3 - S_4 +$

$$
\begin{aligned}
&+{}^{1}/_{6}S_6 - S_7 = 0\\
m_2 :\ & C_2H_4 + {}^{1}/_{2}O_2 - C_2H_4O + {}^{1}/_{2}S_1 - {}^{1}/_{2}S_2 - S_4 - S_7 = 0\\
m_3 :\ & -C_2H_4 - {}^{1}/_{2}O_2 + C_2H_4O - {}^{1}/_{2}S_1 - {}^{1}/_{2}S_2 - S_5 = 0\\
m_4 :\ & 2C_2H_4 + O_2 - 2C_2H_4O + S_1 - S_4 + S_5 - S_7 = 0\\
m_5 :\ & -C_2H_4 - 3O_2 + 2CO_2 + 2H_2O - 3S_1 - 3S_2 - S_3 - S_6 = 0\\
m_6 :\ & {}^{1}/_{3}C_2H_4 + O_2 - {}^{2}/_{3}CO_2 - {}^{2}/_{3}H_2O + S_1 + {}^{1}/_{3}S_3 - S_4 - S_5 + {}^{1}/_{3}S_6 - S_7 = 0\\
m_7 :\ & {}^{5}/_{6}C_2H_4 - C_2H_4O + {}^{1}/_{3}CO_2 + {}^{1}/_{3}H_2O - S_2 - {}^{1}/_{6}S_3 - S_4 - {}^{1}/_{6}S_6 - S_7 = 0\\
m_8 :\ & 5C_2H_4 - 6C_2H_4O + 2CO_2 + 2H_2O - S_3 + 6S_5 - S_6 = 0\\
m_9 :\ & -{}^{5}/_{2}O_2 - C_2H_4O + 2CO_2 + 2H_2O - {}^{5}/_{2}S_1 - {}^{7}/_{2}S_2 - S_3 - S_4 - S_6 - S_7 = 0\\
m_{10} :\ & -{}^{5}/_{2}O_2 - C_2H_4O + 2CO_2 + 2H_2O - {}^{5}/_{2}S_1 - {}^{5}/_{2}S_2 - S_3 + S_5 - S_6 = 0\\
m_{11} :\ & O_2 + {}^{2}/_{5}C_2H_4O - {}^{4}/_{5}CO_2 - {}^{4}/_{5}H_2O + S_1 + {}^{2}/_{5}S_3 - S_4 - {}^{7}/_{5}S_5 +\\
&+{}^{2}/_{5}S_6 - S_7 = 0\\
m_{12} :\ & -S_2 - S_4 - S_5 - S_7 = 0
\end{aligned}
$$

For comparing our above data to Table VII. of [$HOS90$], let us remark that that Table contains mechanisms *only* for the minimal (direct) reactions $d_1$ and $d_3$ and moreover its rows $(m_2, d_3)$ and $(m_3, d_3)$ are identical.

Further, the reaction

$$
{}^{7}/_{6}C_2H_4 + O_2 = C_2H_4O + {}^{1}/_{3}CO_2 + {}^{1}/_{3}H_2O
$$

which can be extracted from our mechanism $m_1$ above is *not* minimal, and in fact it is not listed among the minimal (direct) reactions $d_1$, $d_2$, $d_3$, $d_4$ above we obtainde by running our algorithm with the sum formulas of the terminal (chemical) species. The explanation is, that the vectors $V_1, \ldots, V_5$ are linearly independent which makes the vectors occuring in mechanism $V_1$ a *simplex* !

We computed in the Table 8.5 the lower and upper bounds $(LB, UB)$ according to the formulas of Chapter 4 but only in the case it is applicable (i.e. except from the fourth column).
Again, our formula

$$
\nu(VarAll) = \nu(VarOnly) + \nu(VarOrig)
$$

from (3.5) in subsection 3.2.1 of Chapter 3 can be checked in Table 8.5.

| | Terminal | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|---|
| | species | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 3 | 10 | 10 | 10 |
| $n$ | 3 | 6 | 9 | 9 |
| $M$ | 5 | 7 | 12 | 12 |
| $simp(H)$ | 4 | 1 | 12 | 11 |
| $LB$ | $2 \leq$ | $1 \leq$ | $3 \leq$ | |
| $UB$ | $\leq 5$ | $\leq 1$ | $\leq 66$ | |
| $t$ | $0.00s$ | $0.06s$ | $1.87s$ | $1.80s$ |
| $chk$ | 18 | 102 | $4,000$ | $3,898$ |

$N$ = dimension of the vectorspace
$n$ = dimension of what $H$ spans
$M$ = number of input vectors = $|H|$
$simp(H)$ = number of simplexes
$LB = b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound)
$UB = \binom{M}{n+1}$ (upper bound, if applicable)
$t$ = computational time [sec]
$chk$ = number of checked subsets of $H$

*"Ethylene Oxid"*
**Table 8.5**

# .6 Methane to Methanol Conversion

Our next example is introduced in [*HOS*90] as **Methane to Methanol Conversion**. We are now given the reactions

$S_1 : CH_4 + O_2 = CH_3 + HO_2$
$S_2 : CH_3 + O_2 = CH_3O_2$
$S_3 : CH_3O_2 = CH_2O + OH$
$S_4 : CH_3O_2 + CH_4 = CH_3O_2H + CH_3$
$S_5 : CH_3O_2H = CH_3O + OH$
$S_6 : CH_3O = CH_2O + H$
$S_7 : CH_3O + CH_4 = CH_3OH + CH_3$
$S_8 : OH + CH_4 = CH_3 + H_2O$
$S_9 : CH_3 + CH_3 = C_2H_6$
$S_{10} : CH_3 + OH = CH_3OH$
$S_{11} : CH_3 + CH_3O = CH_3OCH_3$
$S_{12} : CH_2O + CH_3 = CH_4 + CHO$
$S_{13} : CHO + O_2 = CO + HO_2$
$S_{14} : CH_2O + CH_3O = CH_3OH + CHO$
$S_{15} : CHO + CH_3 = CO + CH_4$

where the terminal (chemical) species are $CH_4$, $O_2$, $CH_3OH$, $CO$ and $H_2O$ .

Again the first column of the table below compute all the direct overall reactions among terminal species while the second column deals with the (void) mechanisms among the given reactions $S_1$ through $S_{15}$.

As we indicated in Section 3.2, since only the reactions $S_9$ and $S_{11}$ contain the extra species $C_2H_6$ and $CH_3OCH$, the vectors representing them are linearly independent from the others, so we can omit them and so we can reduce the number and the dimension of the problem by two. For comparison we made computer runs both with the original and with the reduced vectors: these are the two parts of the table below. This reduction helped us to decrease the CPU time from 27 min to 5 min!

The columns in both parts of the table show the various computations as in our previous example 4.5 we explained (the first columns in the two parts are the same).

The output set of mechanisms of the last two columns (i.e. when the input is the reduced set of reaction vectors $S_i$ with $V_1, \ldots, V_5$) is the following:

$m_1 : -2CH_4 - 2O_2 + CH_3OH + CO + 2H_2O + S_1 - 2S_2 - S_3 - S_4 - S_5 - S_7 - 2S_8 - S_{12} - S_{13} = 0$

$m_2 : -2CH_4 - 2O_2 + CH_3OH + CO + 2H_2O + S_1 - 2S_2 - S_3 - S_4 - S_5 - 2S_8 - S_{13} - S_{14} = 0$

$m_3 : -2CH_4 - 2O_2 + CH_3OH + CO + 2H_2O - 2S_2 - S_3 - S_4 - S_5 - S_7 - 2S_8 - S_{12} - S_{15} = 0$

$m_4 : -2CH_4 - 2O_2 + CH_3OH + CO + 2H_2O - 2S_2 - S_3 - S_4 - S_5 - 2S_8 - S_{14} - S_{15} = 0$

$m_5 : -2CH_4 - O_2 + 2CH_3OH - S_2 - S_4 - S_5 - S_7 - S_{10} = 0$

$m_6 : -2CH_4 - O_2 + 2CH_3OH - S_2 - S_4 - S_5 - S_{10} + S_{12} - S_{14} = 0$

$m_7 : -CH_4 - {}^6/_4 O_2 + CO + 2H_2O + S_1 - {}^6/_4 S_2 - S_3 - {}^2/_4 S_4 - {}^2/_4 S_5 - {}^2/_4 S_7 - 2S_8 + {}^2/_4 S_{10} - S_{12} - S_{13} = 0$

$m_8 : -CH_4 \; {}^{-6}/_4 O_2 + CO + 2H_2O + S_1 \; {}^{-6}/_4 S_2 - S_3 \; {}^{-2}/_4 S_4 \; {}^{-2}/_4 S_5 \; {}^{+2}/_4 S_7 - 2S_8 + {}^{+2}/_4 S_{10} - S_{13} - S_{14} = 0$

$m_9 : -2CH_4 - 3O_2 + 2CO + 4H_2O + 2S_1 - 3S_2 - 2S_3 - S_4 - S_5 - 4S_8 + S_{10} - S_{12} - 2S_{13} - S_{14} = 0$

$m_{10} : -CH_4 \; {}^{-6}/_4 O_2 + CO + 2H_2O \; {}^{-6}/_4 S_2 - S_3 \; {}^{-2}/_4 S_4 \; {}^{-2}/_4 S_5 \; {}^{-2}/_4 S_7 - 2S_8 \; {}^{+2}/_4 S_{10} - S_{12} - S_{15} = 0$

$m_{11} : -CH_4 \; {}^{-6}/_4 O_2 + CO + 2H_2O \; {}^{-6}/_4 S_2 - S_3 \; {}^{-2}/_4 S_4 \; {}^{-2}/_4 S_5 \; {}^{+2}/_4 S_7 - 2S_8 \; {}^{+2}/_4 S_{10} - S_{14} - S_{15} = 0$

$m_{12} : -CH_4 \; {}^{-3}/_2 O_2 + CO + 2H_2O \; {}^{-3}/_2 S_2 - S_3 \; {}^{-1}/_2 S_4 \; {}^{-1}/_2 S_5 - 2S_8 \; {}^{+1}/_2 S_{10} \; {}^{-1}/_2 S_{12} \; {}^{-1}/_2 S_{14} - S_{15} = 0$

$m_{13} : 2CH_4 - 3CH_3OH + CO + 2H_2O + S_1 - S_3 + S_4 + S_5 + S_7 - 2S_8 + 2S_{10} - S_{12} - S_{13} = 0$

$m_{14} : 2CH_4 - 3CH_3OH + CO + 2H_2O + S_1 - S_3 + S_4 + S_5 + 2S_7 - 2S_8 + 2S_{10} - S_{13} - S_{14} = 0$

$m_{15} : -2CH_4 + 3CH_3OH - CO - 2H_2O - S_1 + S_3 - S_4 - S_5 + 2S_8 - 2S_{10} + 2S_{12} + S_{13} - S_{14} = 0$

$m_{16} : 2CH_4 - 3CH_3OH + CO + 2H_2O - S_3 + S_4 + S_5 + S_7 - 2S_8 + 2S_{10} - S_{12} - S_{15} = 0$

$m_{17} : 2CH_4 - 3CH_3OH + CO + 2H_2O - S_3 + S_4 + S_5 + 2S_7 - 2S_8 + 2S_{10} - S_{14} - S_{15} = 0$

$m_{18} : 2CH_4 - 3CH_3OH + CO + 2H_2O - S_3 + S_4 + S_5 - 2S_8 + 2S_{10} - 2S_{12} + S_{14} - S_{15} = 0$

$m_{19} : -O_2 - CH_3OH + CO + 2H_2O + S_1 - S_2 - S_3 + S_7 - 2S_8 + S_{10} - S_{13} - S_{14} = 0$

$m_{20} : -O_2 - CH_3OH + CO + 2H_2O + S_1 - S_2 - S_3 - 2S_8 + S_{10} - S_{12} - S_{13} = 0$

$m_{21} : -O_2 - CH_3OH + CO + 2H_2O - S_2 - S_3 + S_7 - 2S_8 + S_{10} - S_{14} - S_{15} = 0$

$m_{22} : -O_2 - CH_3OH + CO + 2H_2O - S_2 - S_3 - 2S_8 + S10 - S_{12} - S_{15} = 0$

$m_{23} : -S_1 + S_{13} - S_{15} = 0$

$m_{24} : \; S_7 + S_{12} - S_{14} = 0$

The computer running which served the above results is summarized in the following table:

**before the reduction:**

| | Terminal | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|---|
| | species | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 3 | 16 | 16 | 16 |
| $n$ | 3 | 13 | 16 | 16 |
| $M$ | 5 | 15 | 20 | 20 |
| $simp(H)$ | 4 | 2 | 24 | 22 |
| $LB$ | $2 \leq$ | $2 \leq$ | $4 \leq$ | |
| $UB$ | $\leq 5$ | $\leq 15$ | $\leq 1140$ | |
| $t$ | $0.00s$ | $30.38s$ | $1353s \approx 22m$ | $1323s \approx 22m$ |
| $chk$ | 18 | $30,473$ | $978,297$ | $947,824$ |

**after the reduction**

| | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|
| | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 14 | 14 | 14 |
| $n$ | 11 | 14 | 14 |
| $M$ | 13 | 18 | 18 |
| $simp(H)$ | 2 | 24 | 22 |
| $LB$ | $2 \leq$ | $4 \leq$ | |
| $UB$ | $\leq 13$ | $\leq 816$ | |
| $t$ | $5.49s$ | $263s \approx 4m$ | $257s \approx 4m$ |
| $chk$ | $7,623$ | $244,611$ | $236,988$ |

$N$ = dimension of the vectorspace
$n$ = dimension of what $H$ spans
$M$ = number of input vectors = $|H|$
$simp(H)$ = number of simplexes
$LB = b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound)
$UB = \binom{M}{n+1}$ (upper bound, if applicable)
$t$ = computational time [sec]
$chk$ = number of checked subsets of $H$

*"Methanol"*
**Table 8.6**

# .7 Glucose to Pyruvate Conversion

Our last example is also taken from [$HOS90$] as **Conversion of Glucose to Pyruvate.** Here the chemical species are abbreviated as

| | |
|---|---|
| $C$ = carbon dioxide | $N = 6 - P$ gluconate |
| $D$ = dihydroxyacetone $P$ | $P$ = pyruvate |
| $E$ = erythrose $4 - P$ | $R$ = ribose $5 - P$ |
| $F$ = fructose $6 - P$ | $S$ = sedoheptulose $7 - P$ |
| $G$ = glucose $6 - P$ | $X$ = xylulose $5 - P$ |
| $K$ = 2-keto-3-deoxy $6 - P$ gluconate | $Y$ = glyceraldehyde $3 - P$ |
| $L$ = ribulose $5 - P$ | |

where the terminal (chemical) species are $G, P$ and $C$.

The original set of reactions is

| | |
|---|---|
| $S_1 : R + X = S + Y$ | $S_8 : N = K$ |
| $S_2 : L = R$ | $S_9 : L = X$ |
| $S_3 : N = L + C$ | $S_{10} : E + X = Y + F$ |
| $S_4 : G = N$ | $S_{11} : Y = P$ |
| $S_5 : F = D + Y$ | $S_{12} : D = P$ |
| $S_6 : G = F$ | $S_{13} : K = Y + P$ |
| $S_7 : D = Y$ | $S_{14} : S + Y = E + F$ |

As we have discussed in Section 3.2 all the six reactions of type $A = \lambda B$ can be omitted with a suitable modification of the remaining others to reduce both dimension and the number of vectors. Let us emphasis here that we have to add the fictive vectors $V_1, V_2, V_3$ *before* this reduction since their coordinates will also be modified. *After* this modification we get the following list of vectors

| $V_1^-$ | $V_2^-$ | $V_3^-$ | $S_1^-$ | $S_3^-$ | $S_5^-$ | $S_{10}^-$ | $S_{13}^-$ | $S_{14}^-$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 1 | 0 | 2 | 1 | 2 | -1 |
| 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 0 | 0 | 1 | -2 | 1 | 0 | -1 | 0 | 0 |
| 1 | 0 | 0 | 0 | -1 | -1 | 1 | -1 | 1 |
| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | -1 |
| 0 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | 1 |

in which the rows correspond to the species $P, C, X, K, S, E$, respectively. This transformation reduced the CPU time from 93 sec to 0.10 sec !

For the Reader's convenience we list here all the *three* sets of output mechanisms: the original one, after the first and after the second reduction (see the 2'nd, 5'th and the last but one columns of Table 8.7 below).

Let us recall that the new vectors $V_1, V_2, V_3$ originally standed for the species $G, P, C$ respectively. However the reduction steps eliminated the speci (row) $G$ while all the remaining vectors were transformed to the vectors $V_1^-, \ldots, S_{14}^-$ .

The original set of (output) mechanisms:

$$
\begin{aligned}
&m_1 : -{}^1\!/_2 G + P + C - S_3 - S_4 + {}^1\!/_2 S_5 + {}^1\!/_2 S_6 + {}^1\!/_2 S_7 - S_9 - S_{13} = 0\\
&m_2 : -G + 2P + C - S_3 - S_4 + S_7 - S_9 - S_{12} - S_{13} = 0\\
&m_3 : -G + 2P + C - S_3 - S_4 - S_9 - S_{11} - S_{13} = 0\\
&m_4 : -{}^1\!/_2 G + P - S_4 + {}^1\!/_2 S_5 + {}^1\!/_2 S_6 + {}^1\!/_2 S_7 - S_8 - S_{13} = 0\\
&m_5 : -G + 2P - S_4 + S_7 - S_8 - S_{12} - S_{13} = 0\\
&m_6 : -G + 2P - S_4 - S_8 - S_{11} - S_{13} = 0\\
&m_7 : -{}^1\!/_2 G + P - {}^1\!/_2 S_5 - {}^1\!/_2 S_6 - {}^1\!/_2 S_7 - S_{11} = 0\\
&m_8 : -{}^1\!/_2 G + P - {}^1\!/_2 S_5 - {}^1\!/_2 S_6 + {}^1\!/_2 S_7 - S_{12} = 0\\
&m_9 : -G + 2P - S_5 - S_6 - S_{11} - S_{12} = 0\\
&m_{10} : C - S_3 - S_4 + S_5 + S_6 + S_7 - S_9 + S_{11} - S_{13} = 0\\
&m_{11} : C - S_3 - S_4 + S_5 + S_6 - S_9 + S_{12} - S_{13} = 0\\
&m_{12} : C - S_3 + S_8 - S_9 = 0\\
&m_{13} : -S_4 + S_5 + S_6 + S_7 - S_8 + S_{11} - S_{13} = 0\\
&m_{14} : -S_4 + S_5 + S_6 - S_8 + S_{12} - S_{13} = 0\\
&m_{15} : S_7 + S_{11} - S_{12} = 0
\end{aligned}
$$

After the first reduction:

$$
\begin{aligned}
&m_1^- : \; -V_1^- + V_2^- + V_3^- - S_3^- = 0\\
&m_2^- : -{}^1\!/_2 V_1^- + 3V_2^- - S_1^- - 3S_3^- + {}^1\!/_2 S_5^- - S_{10}^- - S_{14}^- = 0\\
&m_3^- : -{}^1\!/_2 V_1^- + 3V_2^- - S_1^- - 3S_3^- - S_{10}^- + {}^1\!/_2 S_{13}^- - S_{14}^- = 0\\
&m_4^- : \; {}^5\!/_2 V_1^- - 3V_3^- - S_1^- + {}^1\!/_2 S_5^- - S_{10}^- - S_{14}^- = 0\\
&m_5^- : \; {}^5\!/_2 V_1^- - 3V_3^- - S_1^- - S_{10}^- + {}^1\!/_2 S_{13}^- - S_{14}^- = 0\\
&m_6^- : \; {}^5\!/_2 V_2^- - {}^1\!/_2 V_3^- - S_1^- - {}^5\!/_2 S_3^- + {}^1\!/_2 S_5^- - S_{10}^- - S_{14}^- = 0\\
&m_7^- : \; {}^5\!/_2 V_2^- - {}^1\!/_2 V_3^- - S_1^- - {}^5\!/_2 S_3^- - S_{10}^- + {}^1\!/_2 S_{13}^- - S_{14}^- = 0\\
&m_8^- : \quad S_5^- - S_{13}^- = 0
\end{aligned}
$$

Since two parallel vectors arised after this reduction: $S_5^- \parallel S_{13}^-$ (moreover both of them are of form $A = \lambda B$) we could make a second reduction, this can be seen in the last three columns of Table 8.7. The output set of mechanisms is the following:

$$m_1^= : -V_1^= + V_2^= + V_3^= - S_3^= = 0$$

$$
\begin{array}{ll}
m_2^{=}: & {}^{1}/_{2}V_1^{=} + 3V_2^{=} - S_1^{=} - 3S_3^{=} - S_{10}^{=} - S_{14}^{=} = 0 \\
m_3^{=}: & {}^{5}/_{2}V_1^{=} - 3V_3^{=} - S_1^{=} - S_{10}^{=} - S_{14}^{=} = 0 \\
m_4^{=}: & {}^{5}/_{2}V_2^{=} - {}^{1}/_{2}V_3^{=} - S_1^{=} - {}^{5}/_{2}S_3^{=} - S_{10}^{=} - S_{14}^{=} = 0
\end{array}
$$

This time we did not make any preliminary computation with terminal (chemical) species only.

**original reactions**

| | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|
| | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 13 | 13 | 13 |
| $n$ | 12 | 13 | 13 |
| $M$ | 14 | 17 | 17 |
| $simp(H)$ | 3 | 15 | 12 |
| $LB$ | $2 \leq$ | $4 \leq$ | |
| $UB$ | $\leq 14$ | $\leq 680$ | |
| $t$ | $8.00s$ | $93.00s$ | $85.00s$ |
| $chk$ | $14,600$ | $107,368$ | $92,768$ |

after the **first reduction**

| | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|
| | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 6 | 6 | 6 |
| $n$ | 5 | 6 | 6 |
| $M$ | 6 | 9 | 9 |
| $simp(H)$ | 1 | 8 | 7 |
| $LB$ | $1 \leq$ | $3 \leq$ | |
| $UB$ | $\leq 1$ | $\leq 36$ | |
| $t$ | $0.00s$ | $0.10s$ | $0.10s$ |
| $chk$ | 52 | 418 | 366 |

after the **second reduction :**

| | Reactions | With fictive | vectors $V_i$ |
|---|---|---|---|
| | only | ALL simplexes | WITH $V_i$ only |
| $N$ | 5 | 5 | 5 |
| $n$ | 4 | 5 | 5 |
| $M$ | 4 | 7 | 7 |
| $simp(H)$ | 0 | 4 | 4 |
| $LB$ | $0 \leq$ | $2 \leq$ | |
| $UB$ | $\leq 0$ | $\leq 7$ | |
| $t$ | $0.00s$ | $0.00s$ | $0.00s$ |
| $chk$ | 5 | 65 | 60 |

$N$ = dimension of the vectorspace
$n$ = dimension of what $H$ spans
$M$ = number of input vectors = $|H|$
$simp(H)$ = number of simplexes
$LB = b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ (lower bound)
$UB = \binom{M}{n+1}$ (upper bound, if applicable)
$t$ = computational time [sec]
$chk$ = number of checked subsets of $H$

*"Glucose"*

**Table 8.7**

eof.

Phd-2-d.tex, 2002.10.27., (2002.02.07.),
ScW 3.0 stílusa alapján, Options módosításaival, Ps III