An Algorithmic and Mathematical Investigation of Reactions

Theses of PhD Dissertation

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Introduction

Chemical reactions, like

$$2H_2 + O_2 = 2H_2O \tag{1}$$

occur not single steps, in the reality, rather complicated *sequences* of several **reactionsteps** (**elementary reactions**) in which many intermediate **species** (atomic groups, "rudimentary molecules", as H, H_2, O, O_2, O_3, H_2O, H_2O_2, HO, HO_2) take part. So, (1) is called a **composite reaction**[1)].

Important *tasks to solve*, both for theory and practice, are the following:

I) Find and list all (possible) *elementary* reactions among a given set of species first, and after, find all the *composite* reactions which can be built from the elementary ones.

II) Decompose any given overall reaction like (1) to elementary ones (the reverse of I.)

The problem of finding the final reaction generated by *sequences* of reactions (**mechanisms**) is similar to I. Of course we are interested in *minimal* reactions and mechanisms. Similar problems arise in physics, matroids and hypergraphs.

The huge (exponential) number of elementary reactions and mechanisms makes these problems not so easy even in modern computers.

We take care of mass balance only. Further physical and chemical properties (we call them *evaluating operators*) are discussed in the last Section.

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1) Moreover, chemists discuss *several* models even for the simplest composite reactions like (1). **Tóth,J., Nagy,A.L., Zsély,I.:** *Structural Analysis of Combustion Models (*arXiv:1304.7964 preprint, 2013) introduce and compare some different models.

1. Mathematical definitions, main problems

Fix n atoms, then each species (group of atoms) is represented by a vector from $\mathbb{R}^n$. Reactions are linear combinations of these vectors. Mechanisms are also linear combinations of reactions. We are interested in *minimal* reactions (mechanisms), so these vectors must form a *minimal dependent* set.

Definition 1 ***(PhD 1.7.D.)*** *Any $S \subset \mathbb{R}^n$ is a* ***(linear algebraic) simplex*** *if it is* minimal dependent, *i.e. S is (linearly) dependent but all of its proper subsets are independent.* □

Geometric and *affine* simplexes are defined in PhD 1.9.D.-1.11.D. (below 40.D), relations among different kinds of simplexes are discussed in PhD 4.18.D., 4.19.Á. (below 38.D, 39.S) and in [2012b]. The main properties of *linear algebraic* simplexes are discussed in PhD Subsection 1.5.

We omit the adjective *linear algebraic* in what follows.

Notation 2 *Any dependent set $S = \{\mathbf{b}_1, ..., \mathbf{b}_k\} \subset \mathbb{R}^n$ corresponds to a homogeneous system of linear equations*

$$\sum_{j=1}^{k} x_j \cdot \mathbf{b}_j = \mathbf{0} \tag{2}$$

which has a nontrivial solution $\mathbf{x} = [x_1, ..., x_k] \in \mathbb{R}^k$. □

In the dissertation we deal with the following problems (Subsection 1.6):

Problem 3 ***(PhD 1.22.P.)*** *Reveal the structure of the solutions of (2) in details for S* simplexes.

Problem 4 ***(PhD 1.23.P.)*** *Fix any vectors $\mathbf{a}_1, ..., \mathbf{a}_m \in \mathbb{R}^n$. Construct all solutions of the homogeneous system $\sum_{j=1}^{m} x_j \cdot \mathbf{a}_j = \mathbf{0}$ if the solutions of the systems $\sum_{\mathbf{a}_j \in S} x_j \cdot \mathbf{a}_j = \mathbf{0}$ for $S \subsetneqq \{\mathbf{a}_1, ..., \mathbf{a}_m\}$ simplexes are known.*

Problem 5 ***(PhD 1.24.P.)*** *Construct a fast algorithm which finds all simplexes $S \subseteq H$ for any given $H = \{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_m\} \subset \mathbb{R}^n$.*

The number of simplexes in H is a critical point for any algorithm:

Problem 6 ***(PhD 1.25.P.)*** *Give* ***lower*** *and* ***upper*** *bounds for the number of simplexes, contained in m-element sets $H \subset \mathbb{R}^n$ for H spanning $\mathbb{R}^n$.*

Parallel vectors (isomers, multiple doses) play a negative role in lower bounds (see Theorem 34), so we deal separately with the case when no parallel vectors are in H :

Problem 7 ***(PhD 1.26.P.)*** *The same as Problem 6 but H must not contain parallel vectors.*

The methods of treating to Problems 6 and 7 suggest to look for more general structures:

Problem 8 ***(PhD 1.27.P.)*** *Give the equivalent notion of simplexes in* matroids *and give* ***lower*** *and* ***upper*** *bounds for the number of simplexes, contained in an m -element set H in a matroid.*

Problem 9 ***(PhD 1.28.P.)*** *Give the equivalent notion of simplexes in* hypergraphs *and give* ***lower*** *and* ***upper*** *bounds for the number of simplexes, contained in an m -element set H in a hypergraph.*

Atoms-species-mechanisms ... form a kind of hierarchy since the inputs of the higher level are exactly the outputs of the lower one.

Problem 10 ***(PhD 1.29.P.)*** *Give a mathematical definition of* ***stoichiometric hierarchy,*** *study its properties and relations to physics and chemistry.*

Problem 11 *Study the properties of species and reactions other than linear combinations.*

2. The algorithm and its variations

Problem 5 and its applications are studied in this Section ([1991], [2000a]).

The algorithm

Each simplex in $\mathbb{R}^n$ has size at most $n+1$ and a set H of m vectors may have at most $\sum_{i=1}^{n+1}\binom{m}{i} = \binom{m+1}{n+2} - 1 = \mathcal{O}\left(m^{n+2}\right) \quad (m \to \infty)$ such subsets. However we do not have to check these m^{n+2} subsets, since

Proposition 12 *All subsets of independent sets are independent, too.* $\square$

Our algorithm, introduced in the dissertation Section 2.1 decreases the number of subsets of H to be investigated (PROCEDURE MODIFY) to m^{n+1}. The subsets of H are checked in the *lexicographic order*, combined with a "back and forth" direction. Details can be founf in subsections 2.1 and 2.5.

The algorithm is applicable in any hypergraph which posseses a property similar to Proposition 12:

Definition 13 ***(PhD 2.4.D.) (i)*** *A hypergraph* $\mathcal{H} = (V, \mathcal{E})$ *is* ***descending*** *if* $E, F \subseteqq V$, $E \in \mathcal{E}$ *and* $F \subset E$ *implies* $F \in \mathcal{E}$ *,*
(ii) $\mathcal{H}$ ***is not deformed*** *if* $\{v\} \in \mathcal{E}$ *for each* $v \in V$*,*
(iii) *assumed (i) and (ii), the elements of* $\mathcal{E}$ *are called* ***independent****,*
(iv) $S \subseteqq V$ *is a* ***simplex*** *if* $S \notin \mathcal{E}$ *but for each* $T \subsetneqq S$ *we have* $T \in \mathcal{E}$ *.* □

Theorem 14 ***(PhD 2.2.T.) (i)*** *The algorithm does not miss any simplex and does not check any subset twice.*
(ii) *The running time of the algorithm is the best possible for any dataset, that is it checks the neccessary ones only.* □

Theorem 15 ***(PhD 2.3.T.)*** *For any* $H \subset \mathbb{R}^n$, $|H| = m$ *the algorithm checks at most* m^{n+1} *subsets of* H *, so the time elapsed is* $\mathcal{O}(m^{n+1})$*, the algorithm is polynomial in time.* □

Computer examples are shown in the last Section of the dissertation: for some dozens of vectors in dimension $10 - 20$ we have result in some seconds.

The time $\mathcal{O}(m^{n+1})$ can not be decreased in general, by Theorem 32 and Corollary 33.

Extensions and applications

By minor modifications of the *input* and careful investigations of the *output* many other problems can be resolved, too (PhD subsection 2.2, [2000a]).

Reducing the dimension

(a) Drop the vectors independent from the other. This is a $\mathcal{O}(m^2)$ time check before running but can save $\mathcal{O}(m^n)$ time.
(b) *If* a vector has exactly *two* nonzero coordinates, then we can delete this vector *and* we can decrease the dimension by 1 for *all* the remaining vectors. In chemical language: in the presence of a reaction $A = \lambda B$ we may "substitue" the species A by λB for calculations and, after running the algorithm, use again the species A . Of course we have to find all mechanisms $\mathcal{M}$ of the original problem. The details can be found in subsection 2.2.0, the running time in Example 7.7 falled from 93 sec to 0.01 sec.

Searching direct reactions

Let us given the reactions $X_1, ..., X_k \in \mathbb{R}^N$ which contain both *terminal species* (reactants) and *nonterminal* (intermediate) ones. Find the mechanisms $Y = \sum_{i=1}^{k} \lambda_i X_i$ such that the overall reaction $\mathbf{Y} = \mathcal{R}(\underline{\lambda})$ contain terminas species only, where $\mathbf{Y}$ is unknown. In Subsection 2.2.1 two equivalent solutions are given to this problem.

Searching direct mechanisms

We are given one (or more) reaction $\mathbf{R}$ and we have to find the *minimal* mechanisms $\mathcal{M}$ resulting $\mathbf{R}$. To solve this we add $\mathbf{X}_{k+1} := \mathbf{R}$ to the given set $H := \{\mathbf{X}_1, ..., \mathbf{X}_k\}$ and search only the simplexes which contain $\mathbf{R}$. From the equality $\sum_{j=1}^{k+1} \lambda_j \cdot \mathbf{X}_j = \mathbf{0}$ we get $\mathcal{M} := \frac{-1}{\lambda_{k+1}} \sum_{j=1}^{k} \lambda_j \cdot \mathbf{X}_j$ since all each $\lambda_j \neq 0$. See subsection 2.2.2 for details.

Neither terminal species nor reactions are known

We do not know the terminal species but we have to find *all* overall reactions. Simply running the original algorithm we can extract all overall reactions from the output, as described in subsection 2.2.3.

In Section 7 we show several computer experiments with explanations.

Detailed comparison of our algorithm and methods to other author's ones can be found in subsection 2.4.

Thesis I

i) A *polinomial time algorithm* was developed for listing all simplexes contained in any given set $H \subset \mathbb{R}^n$ (moreover, in any $H \subsetneqq V$ where $\mathcal{H} = (V, \mathcal{E})$ is a descending, not deformed hypergraph) in lexicographical order (Subsection 2.1, [1991]).

ii) It was proved, that the algorithm finds the simplexes *in the fewest steps for any dataset* $H \subsetneqq \mathbb{R}^n$ (PhD 2.2.T. and 2.3.T).

iii) It was revealed, that *reducing the dimension* of the data in H can save up to 90% of running time in certain cases (Subsection 2.2.0).

iv) *Extensions of the algorithm* for finding direct reactions and mechanisms were given, even in the case when both terminal species and reactions are unknown (Subsections 2.2.1, 2.2.2 and 2.2.3, [2000a]).

v) An *implementation of the algorithm* in Pascal was contructed and *several runs* were made for problems we found in the literature, our outputs were compared to other authors' results (Subsections 2.4 and 7). ■

3. Systems of linear equalities

Now we deal Problems 3 and 4 ([2012a],[2012b]). We have far different answers to homogeneous and inhomogeneous systems.

Notation 16 *$M_{A,\underline{b}}$ and $M_{A,\underline{0}}$ denote the sets of solutions of the systems of linear equations $A{\cdot}\underline{x} = \underline{b}$ and $A{\cdot}\underline{x} = \underline{0}$ ($A \in \mathbb{R}^{n\times m}$, $\underline{b} \in \mathbb{R}^n$), resp. The column vectors of A are denoted by $\underline{a}_1, \underline{a}_2, \ldots, \underline{a}_m \in \mathbb{R}^n$, i.e. $A = [\underline{a}_1, \underline{a}_2, \ldots, \underline{a}_m]$.* □

Condition 17 ***(PhD 3.2.F.) o)*** *$M_{A,\underline{0}} \neq \{\underline{0}\}$ and $|M_{A,\underline{b}}| > 1$,*
i) *A has no parallel columns, especially*
ii) *A has no column $\underline{0}$,*
iii) *A has no column parallel to $\underline{b}$.* □

Definition 18 ***(PhD 3.3.D.) (i)*** *For any $\underline{x} \in \mathbb{R}^m$ let*

$$\mathbf{supp}\,(\underline{x}) := \{i \leq m : x_i \neq 0\} \tag{3}$$

the ***support*** *of $\underline{x}$, especially* $\mathbf{supp}\,(\underline{0}) = \emptyset$.

(ii) *For any $M \subseteq \mathbb{R}^m$ the vector $\underline{z} \in M$, $\underline{z} \neq \underline{0}$ has a* ***minimal support*** *with respect to M if there is* no *$\underline{y} \in M$, $\underline{y} \neq \underline{0}$ such that supp $(\underline{y}) \subsetneqq$ supp $(\underline{z})$. In this case we say $\underline{z} \in M$ is* ***minimal*** *(to M).*

(iii) *For any $M \subseteq \mathbb{R}^m$*

$$M^{\min} := \{\underline{z} \in M : \underline{z} \text{ is minimal to } M \} \ . \tag{4}$$

(iv) *$M^{\min}_{A,\underline{b}}$ and $M^{\min}_{A,\underline{0}}$ are defined for $M_{A,\underline{b}}$ and $M_{A,\underline{0}}$, the elements of $M^{\min}_{A,\underline{b}}$ and $M^{\min}_{A,\underline{0}}$ are called* ***minimal solutions*** *of $A \cdot \underline{x} = \underline{b}$ and $A \cdot \underline{x} = \underline{0}$.* □

The connection and differences of *minimal* and *base* solutions are discussed in Remark 30 (PhD 3.18.M.).

Proposition 19 ***(PhD 3.17.Á.)*** *For any $\underline{z} \in M^{\min}_{A,\underline{0}}$ the relevant set of column vectors of A in the equality $A \cdot \underline{z} = \underline{0}$,*

$$S_{\underline{z}} := \{\underline{a}_i : i \in supp\,(\underline{z})\} \subset \mathbb{R}^n \tag{5}$$

is a minimal *dependent set, i.e. a simplex.* □

Definition 20 ***(PhD 3.7.D.)*** *For $\underline{x} \in \mathbb{R}^m$, $A \in \mathbb{R}^{n\times m}$ and $H \subseteq \{1, \ldots, m\}$, $|H| = h$ the* ***resctrictions*** *of $\underline{x}$ and A to the set H is*

$$\begin{aligned} \underline{x}\mid_H \ &: = [x_i : i \in H] \in \mathbb{R}^h \\ A\mid_H \ &: = [\underline{a}_i : i \in H] \in \mathbb{R}^{n\times h} \ . \end{aligned} \tag{6}$$

□

Homogeneous systems

Theorem 21 ***(PhD 3.10.T.)*** *For any* $\underline{z} \in M^{\min}_{A,\underline{0}}$ *,* $\underline{z} \neq \underline{0}$ *the equality*

$$\left(A\mid_{supp(\underline{z})}\right) \cdot \underline{y} = \underline{0} \tag{7}$$

has a unique *(up to a constant multiplier) solution* $\underline{y} \in \mathbb{R}^h$ *(*$h = |supp\,(\underline{z})|$*), namely*

$$\underline{y} = \lambda \cdot \underline{z}\mid_{supp(\underline{z})} \quad (\lambda \in \mathbb{R}) \qquad \square \tag{8}$$

See also PhD 1.17.T., 3.19.K., 3.21.K. and 3.22.Á.

Theorem 22 ***(PhD 3.20.T.)*** *For any* $A \in \mathbb{R}^{n\times m}$ *with column vectors* $\underline{a}_1, \underline{a}_2, \ldots, \underline{a}_m$ *and for any* simplex $S \subseteqq \{\underline{a}_1, \underline{a}_2, \ldots, \underline{a}_m\}$ *there is a (unique) solution* $\underline{x}$ *of the homogeneous equation* $A\underline{x} = \underline{0}$ *which uses exactly the elements of* S *, i.e.*

$$S = \{\underline{a}_i : i \in supp\,(\underline{x})\} \ . \qquad \square \tag{9}$$

Now the solution of Problem 4 is:

Theorem 23 ***(PhD 3.13.T.)*** $M^{\min}_{A,\underline{0}} \subseteqq \mathbb{R}^m$ *generates* $M_{A,\underline{0}} \subseteqq \mathbb{R}^m$ *for any* $A \in \mathbb{R}^{n\times m}$*.* $\square$

Corollary 24 ***(PhD 3.15.K.)*** *For any* $\underline{x} \in M_{A,\underline{0}}$

$$supp\,(\underline{x}) \subseteqq \bigcup \left\{supp\,(\underline{z}) : \underline{z} \in M^{\min}_{A,\underline{0}}\right\} \ . \quad \square \tag{10}$$

Remark 25 $M^{\min}_{A,\underline{0}}$ *may contain dependent but not parallel elements. To reveal a* base *of* $M^{\min}_{A,\underline{0}}$ *would be interesting.* $\square$

Inhomogeneous systems

Theorem 26 ***(PhD 3.23.T.)*** *For any* $\underline{z} \in M^{\min}_{A,\underline{b}}$ *and* $H := supp\,(\underline{z})$

$$(A\mid_H) \cdot \underline{y} = \underline{b} \tag{11}$$

has the only solution $\underline{y} = \underline{z}\mid_H$ *.* $\square$

A generalization and solution of Problem 4 is:

Problem 27 ***(PhD 3.24.P.)*** *Can* ***all*** *solutions of* $A \cdot \underline{x} = \underline{b}$ *be generated from the* minimal *solutions, i.e. from the elements of* $M^{\min}_{A,\underline{b}}$ *?*

Theorem 28 ***(PhD 3.25.T.)*** *Each solution* $\underline{x} \in M_{A,\underline{b}}$ *is an* affine *linear combination of the elements* $M^{\min}_{A,\underline{b}}$ plus *one solution of* $A \cdot \underline{x} = \underline{0}$ *, i.e.*

$$\underline{x} = \sum_{i=1}^{I} \alpha_i \underline{z}_i + \underline{y} \qquad ahol \qquad \sum_{i=1}^{I} \alpha_i = 1 \tag{12}$$

where $\underline{z}_i \in M^{\min}_{A,\underline{b}}$ *and* $\underline{y} \in M_{A,\underline{0}} \cup \{\underline{0}\}$ *.* □

Corollary 29 ***(PhD 3.26.K.)*** $M^{\min}_{A,\underline{b}} \cup M^{\min}_{A,\underline{0}}$ *generates* $M_{A,\underline{b}}$ □

This is a generalization of the wellknown relation $M_{A,\underline{b}} = \underline{z} + M_{A,\underline{0}}$.

Remark 30 ***(PhD 3.18.M.)*** Connection of minimal- and base solutions:
Inhomogeneous *systems: a base solution* $\underline{x}$ *corresponds to a base of* A *but some components of* $\underline{x}$ *may be* 0 *. So* $\underline{x}$ *is* minimal iff *it is* nondegenerate*.*
Homogeneous *systems: each base solution refers to a* base *of* A and *a further columns of* A *, this is an* $r+1$ *-element dependent vectorset where* r *is the rank of* A *. Such set need not be a simplex (PhD 1.8.M.). On the other hand: minimal solutions* $\underline{x}$ *correspond to simplexes, and they are base solutions exactly when supp* (x) *has the size* $r+1$ *.* □

Thesis II

i) A thoroughful investigation of the *structure of sets of minimal solutions* both of homogeneous and inhomogeneous sets of linear equalities was done. We also revealed the *connection* of these solutions to the simplexes and the uncostrained solutions (Section 3, [2012b]).

ii) Namely, *in the homogeneous case* the minimal solutions (elements of $M^{\min}_{A,\underline{0}}$) generate all the solutions (PhD 3.13.T.). *In the inhomogeneous case* all solution can be written as the sum of an *affine* combination of some elements of $M^{\min}_{A,\underline{b}}$ plus one element of $M_{A,\underline{0}}$ (PhD 3.25.T.).

iii) The relations between *minimal- and base solutions* is explained in PhD 3.18.R. ■

4. The number of simplexes in $\mathbb{R}^n$

Here we deal with Problems 6 and 7 ([1995], [1998], [2011]).

Notation 31 ***(PhD 4.2.J.)*** **simp** (H) *denotes the* ***number*** *of simplexes in* $H \subset \mathbb{R}^n$. □

The maximum

A set of simplexes form a **Sperner-family,** so Sperner's well known theorem gives an upper bound for *simp* (H). However we are interested in the structure of the extremal sets H.

Theorem 32 ***(PhD 4.5.T.***,*[1995])* *For any* $H \subset \mathbb{R}^n$ *of fixed size and spanning* $\mathbb{R}^n$, $simp(H)$ *is* ***maximal*** if and only if *any* n *elements of* H *are independent.* □

Corollary 33 ***(PhD 4.6.K.)*** *For any* $H \subset \mathbb{R}^n$, *spanning* $\mathbb{R}^n$ *and having* m *element*

$$simp(H) \leq \binom{m}{n+1} \quad , \tag{13}$$

and the bound is sharp. □

So the atoms must form species "randomly" (or like a Vandermonde-determinant) in order to be able to form the most possible number of reactions.

The minimum, allowing parallel vectors

Theorem 34 ***(PhD 4.7.T.***,*[1995])* *For any* $H \subset \mathbb{R}^n$ *of fixed size and spanning* $\mathbb{R}^n$, $simp(H)$ *is* ***minimal*** if and only if H *consists of* n *collections of parallel vectors of sizes differing by at most one from each other.*

In case $|H| \geq 2n$ *this is the* unique *configuration for containing minimum simplexes.* □

Corollary 35 ***(PhD 4.12.K.)*** *For any* $H \subset \mathbb{R}^n$ *spanning* $\mathbb{R}^n$ *and* $|H| = m = an + b$ $(0 \leq b < n)$ *we have*

$$b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(H) \ , \tag{14}$$

and this bound is sharp. If m *is divisible by* n *we have*

$$n \cdot \binom{\frac{m}{n}}{2} \leq simp(H) \ . \qquad \Box \tag{15}$$

For $n+1 \leq m < 2n-1$ we have many other minimal configurations:

Example 36 ***(PhD 4.14.P.)*** *Let* $n+1 \leq m < 2n-1$, *fix a base* $\mathcal{K} = \{\underline{e_1}, ..., \underline{e_n}\} \subset \mathbb{R}^n$ *and let* $\Pi = \{\mathcal{I}_1, ..., \mathcal{I}_\ell\}$ *be any partition of* $\mathcal{K}$, $|\mathcal{I}_j| \geq 2$ *and*

$m = n + \ell < 2n - 1$. *Let* $\underline{v_j} := \sum_{i \in \mathcal{I}_j} \mu_i \underline{e_i}$ *for* $j \leq \ell$ *be* any *vector where* $\mu_i \neq 0$. *The sets*

$$S_j := \mathcal{I}_j \cup \left\{ \underline{v_j} \right\} \qquad (j \leq \ell)$$

are all simplexes by PhD 1.15.S., and so the set

$$H_\Pi = \left\{ \underline{e_1}, ..., \underline{e_n} \right\} \cup \left\{ \underline{v_1}, ..., \underline{v_\ell} \right\}$$

contains ℓ *many simplexes and* $|H_\Pi| = n + \ell = m$ *.* □

Thesis III

i) The *general sharp upper bound* for the number of simplexes contained in sets $H \subset \mathbb{R}^n$ of given size ($|H| = m$) was found: $simp(H) \leq \binom{m}{n+1}$, assuming H spans $\mathbb{R}^n$. Moreover, the *unique structure of the extremal sets* H is also described (PhD 4.5.T., [1995]).

ii) General *sharp lower bound* was found: $b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2} \leq simp(H)$ where $m = a \cdot n + b$, $0 \leq b < n$. We proved, that *the structure of the extremal sets* for $m \geq 2n$ is *unique* (PhD 4.7.T., [1995]). ■

The minimum without parallel vectors

As we have seen, the lower bound is achieved only when H contains of parallel vectors only. What about other sets, satisfying the following condition:

Condition 37 ***(PhD 4.16.F.)*** $H \subset \mathbb{R}^n$ *does* not *contain parallel elements (esp.* $\underline{0} \notin H$*).* □

Reducing the dimension

Substituting the elements of H with the set of their scalar multipliers and intersecting these sets with a suitable hyperplane of $\mathbb{R}^n$ we can transform our problem to $\mathbb{R}^{n-1}$:

Definition 38 ***(PhD 4.18.D.)*** *For any* $\underline{h} \in \mathbb{R}^n$ *and* $H \subset \mathbb{R}^n$ *we let*

$$\Lambda \underline{h} := \{ \lambda \cdot \underline{h} : \lambda \in \mathbb{R},\ \lambda \neq 0 \} \ , \quad \Lambda H := \{ \Lambda \underline{h} : \underline{h} \in H \} \ ,$$

and for any $n-1$ *-dimensional hyperplane* $\mathcal{P} \subset \mathbb{R}^n$*, not parallel to any element of* H *we let* $H^{\mathcal{P}} := \Lambda H \cap \mathcal{P}$ *.* □

We identify $\mathcal{P}$ to $\mathbb{R}^{n-1}$. For any simplex $S \subset \mathbb{R}^n$ we know that $S^{\mathcal{P}} \subset \mathbb{R}^{n-1}$ is an *affine* simplex (see PhD 1.10.D. and 1.11.D.).

Proposition 39 ***(PhD 4.19.Á.)*** *There is a bijection between* $H^{\mathcal{P}}$ *and* H*, similarly between the* affine *simplexes of* $H^{\mathcal{P}}$ *and the* linear algebraic *simplexes of* H *, implying*

$$\left|H^{\mathcal{P}}\right| = |H| \quad \textit{and} \quad simp_a\left(H^{\mathcal{P}}\right) = simp_\ell\left(H\right) \tag{16}$$

where $simp_a\left(H^{\mathcal{P}}\right)$ *denotes the* ***number*** *of affine simplexes in* H *.* □

(See subsection 4.3.1.) The cases $n = 3$ and $n = 4$ are visible:

Definition 40 ***(PhD 1.11.D) (i)*** *A set of points* $S \subset \mathbb{R}^2$ *is an* ***affine***
▷ 3 *-element* ***simplex*** *iff* S *is three colinear points,*
▷ 4 *-element simplex iff* S *is any four points but none three of them are colinear,*
▷ *there are no other affine simplexes in* $\mathbb{R}^2$*.*

Example 41 ***(ii)*** *A set of points* $S \subset \mathbb{R}^3$ *is an* ***affine***
▷ 3 *-element* ***simplex*** *iff* S *is three colinear points,*
▷ 4 *-element simplex iff* S *is any four coplanar points but none three of them are colinear,*
▷ 5 *-element simplex iff* S *is any five points but none four are coplanar (and thus none three of them are colinear),*
▷ *there are no other affine simplexes in* $\mathbb{R}^3$*.* □

The number of simplexes in $\mathbb{R}^3$

Theorem 42 ***(PhD 4.20.T.,****[1998]**)*** *For any* $H \subseteq \mathbb{R}^3$ *of fixed size not equal to* 3*,* 4 *or* 7*, such that* H *spans* $\mathbb{R}^3$ *and* no parallel vectors *are allowed in* H *,* $simp(H)$ *is minimal if and only if* H *is contained in two intersecting planes (their intersection vector belongs to* H*), one of which is of size* 3*. In other words: precisely when* H *contains* 3 *linearly independent vectors* $\{u_1, u_2, u_3\}$*, another vector* v *colinear with* u_1 *and* u_2 *and the rest* $H \setminus \{u_1, u_2, u_3, v\}$ *colinear with* u_2 *and* u_3 *.* □

Equivalently, talking about points on the plane:

Theorem 43 ***(PhD 4.20.T.)*** *For any* $H \subseteq \mathbb{R}^2$ *of fixed size not equal to* 3*,* 4 *or* 7*, such that* H *is not contained in a line,* $simp_a(H)$ *is minimal exactly when* H *is contained in two intersecting lines and one of this lines contains exactly three elements of* H *.* □

Corollary 44 ***(PhD 4.22.K.)*** *If $H \subseteq \mathbb{R}^3$, H spans $\mathbb{R}^3$, $|H| = m \geq 8$ and* no parallel vectors *are allowed in H, then we have the sharp bounds*

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

See Subsection 4.3.2 for $|H| < 8$.

The number of simplexes in $\mathbb{R}^4$

Theorem 45 ***(PhD 4.23.T.***, [2011]***)*** *Assuming $H \subset \mathbb{R}^4$, no parallel vectors are in H but H spans $\mathbb{R}^4$ and H has given size at least 24, $simp_\ell(H)$ is minimal* exactly when *H is contained in two disjoint 2-dimensional planes, and the difference of the numbers of vectors of H contained in these planes is at most 1.* $\square$

Equivalently:

Theorem 46 ***(PhD 4.24.T.)*** *For any $H \subseteq \mathbb{R}^3$ of fixed size $|H| = m \geq 24$, such that H is not contained in a plane, $simp_a(H)$ is minimal exactly when H is contained in two skew (detour) lines and these lines contain $\lfloor m/2 \rfloor$ and $\lceil m/2 \rceil$ many points of H .* $\square$

Corollary 47 ***(PhD 4.25.K.)*** *Assuming $H \subset \mathbb{R}^4$, no parallel vectors are in H, H spans $\mathbb{R}^4$ and $|H| = m \geq 24$, we have the sharp bound*

$$\binom{\lfloor m/2 \rfloor}{3} + \binom{\lceil m/2 \rceil}{3} \leq simp\,(H) \ . \quad \square$$

We plan to check the cases $4 \leq |H| \leq 23$ by a computer.

Further problems and conjectures

Problem 7 for $n \geq 5$ is unsolved. We have the following conjecture:

Conjecture 48 ***(PhD 4.27.S.,[1998])*** *In the case of $H \subset \mathbb{R}^n$, H spans $\mathbb{R}^n$ and no parallel vectors are allowed in H ,the minimum for $simp\,(H)$ is attained precisely for the following configurations:*
(i) *if n is even, then H contains n linearly independent vectors $\{u_i : i = 1, \ldots, n\}$ and the remaining divided as evenly as possible between the planes $\{[u_i, u_{i+1}]; i = 1, 3, \ldots, n-1\}$,*
(ii) *if n is odd, then H again contains n linearly independent vectors $\{u_i : i = 1, \ldots, n\}$, one special vector in the plane $[u_{n-1}, u_n]$ and finally the remaining vectors divided as evenly as possible between the planes $\{[u_i, u_{i+1}]; i = 1, 3, \ldots, n-2\}$ with lower indices having precedence.* $\square$

The following strenghtening of Problem 7 is also interesting in the practice: consider only the (complicated) reactions involving at least k many species:

Problem 49 ***(PhD 4.28.P.) version a)*** *For any $n, m, k \in \mathbb{N}$ and $H \subset \mathbb{R}^n$, H spans $\mathbb{R}^n$, $|H| = m$ find the minimal value of $simp_k(H)$ = the number of k-element simplexes, and what are the extremal sets,*
version b) *the same as a) but assuming that H does not contain simplexes of size smaller than k .* □

See also Conjectures 69 and 72 below. One modification of our algorithm (subsection 2.2) asks:

Problem 50 ***(PhD 4.29.P.)*** *For any given $\mathcal{V} := \{\underline{v_1}, \ldots, \underline{v_t}\} \subset \mathbb{R}^n$ and $m \in \mathbb{N}$ calculate (minimum and maximum) $simp_{\mathcal{V}}(H)$, the number of simplexes $S \subset H$ satisfying $S \cap \mathcal{V} \neq \emptyset$, for $H \subset \mathbb{R}^n$, $|H| = m$ and H spans $\mathbb{R}^n$. What are the extremal sets H ?* □

Thesis IV

i) Assuming that H does not contain paralel elements, we reduced first the dimension of the elements in H (Subsection 4.3.1).

ii) In the case $H \subset \mathbb{R}^3$, $|H| \geq 8$ and H does not contain paralel elements *we gave the sharp lower bound* for *simp*(H) and we also determined *the unique structure of the extremal sets $H \subset \mathbb{R}^3$* which span $\mathbb{R}^3$ (PhD 4.20.T., [1998]).

iii) In the case $H \subset \mathbb{R}^4$ and H does not contain paralel elements *we gave the sharp lower bound* for *simp*(H) for $|H| \geq 24$, and we also determined *the unique structure of the extreme sets $H \subset \mathbb{R}^4$* of full dimension (PhD 4.23.T, [2011]). ■

5. Matroids and hypergraphs

Problems 8 and 9 are dealt here.

Notation 51 *m denotes the **size** and n the **rank** of the matroid $\mathcal{M} = (X, \mathcal{F})$, $0 < n < m$.* □

The maximum in matroids

Using **Construction 1** we can prove:

Theorem 52 ***(PhD 5.4.T.)*** *In the case $m = n + 1$ any matroid contains exactly one* circle. *When $m > n+1$, only the uniform matroid $U_{m,n}$ contains the most circles, $\binom{n+1}{m}$ many.* □

Theorem 53 ***(PhD 5.7.T.)*** *Only $U_{m,n}$ contains maximum number* bases*: $\binom{m}{n}$ many.* □

The minimum in matroids

Theorem 54 ***(PhD 5.8.T.)*** *When allowing loops, for any $m, n \in \mathbb{N}$ there is a* unique *matroid $\mathcal{M}_o^{(m,n)}$ containing only* one base*.* □

Theorem 55 ***(PhD 5.9.T.)*** *Any matroid $\mathcal{M}$ contains at least $n-m$ many* circles*. $\mathcal{M}$ has only $n-m$ many circles if and only if all circles of $\mathcal{M}$ are disjoint.* □

Remark 56 ***(PhD 5.10.T.)*** *The circles of $\mathcal{M}_o^{(m,n)}$ (defined in 54.) are disjoint, too.* □

We use **Construction 2** when loops are not allowed.

Theorem 57 ***(PhD 5.13.T.)*** *Let $\{a_1, a_2, \ldots, a_n\}$ be a fixed base of $\mathcal{M}$ where $\mathcal{M}$ contains neither loops nor large circuits. Denote ϑ_i the number of elements parallel to a_i (including also a_i). Then $\mathcal{M}$ contains minimal number of circles exactly when $|\vartheta_i - \vartheta_j| \leq 1$ for all $i \neq j$* **.** □

Corollary 58 ***(PhD 5.14.K.)*** *Any matroid* without loops *contains at least $b \cdot \binom{a+1}{2} + (n-b) \cdot \binom{a}{2}$ many circuits ($m = an + b$, $0 \leq b < n$).* □

The *structure* of the extremal matroids is unique for $m \geq 2n$.

Theorem 59 ***(PhD 5.15.T.)*** *Loopless matroids contain minimum number of* circles *if and only if*
a) *in case $m < 2n$ the circles are pairwise disjoint,*
b) *in case $m \geq 2n$ there are 2-element circuits (parallel elements) only and these parallel-classes differ in size by at most 1 .* □

Theorem 60 ***(PhD 5.21.T.)*** *Loopless matroids contain minimum number of* bases *if and only if it has a base $\{a_1, a_2, \ldots, a_n\}$ such that all other elements are parallel to a_1 .* □

Corollary 61 ***(PhD 5.23.K.)*** *Loopless matroids contain al least $m-n+1$ many bases, the extremal structure is unique.* □

Subsection 5.5 contains several open questions on matroids.

Hypergraphs

For hypergraphs first we have to define the problem itself. In the dissertation we present a simple version, a more general case is discussed in [2013a].

Definition 62 ***(PhD 5.24.,5.25.D.)*** *For any hypergraph* $\mathcal{H} = (V, \mathcal{E})$, $V \neq \emptyset$ *and* $k \in \mathbb{N}$ *we define*
(i) $\mathcal{E}_k := \{E \in \mathcal{E} \ : \ |E| = k\}$,
(ii) *any* k*-element subset of* V *is* k***-vertex,***
(iii) $S \subset V$ *is* ***in general position*** *if*

$$S \nsubseteq E \quad \textit{for all } E \in \mathcal{E} \ , \tag{17}$$

(iv) S *is* k***-pyramid*** *if it is a* k*-vertex in general position,*
(v) 4*-vertices are* ***quads***, 4*-pyramids are* ***tetrahedrons***,
(vi) $S \subset V$ *is a* 4*-element* ***simplex*** *if it is a quad but not a tetrahedron:*

$$S \subseteq E \quad \textit{for some } E \in \mathcal{E} \ , \tag{18}$$

$\mathcal{S}_4$ *is the* set *of the* 4*-element simplexes,*

(vii) $T \subset V$ *is a* 5*-element* ***simplex*** *if it is a* 5*-vertex but no its subset is a* 4*-element simplex:*

$$F \nsubseteq T \quad \textit{for all } F \in \mathcal{S}_4 \ , \tag{19}$$

or in other words: $|T \cap E| \leq 3$ *for* $E \in \mathcal{E}$, $\mathcal{S}_4$ *is the* set *of the* 5*-element simplexes.* □

Condition 63 ***(PhD 5.27.,5.29.F.)*** ***i)*** $\mathcal{E}_\ell = \emptyset$ *for* $\ell \leq 3$,
ii) *for any* $E_1, E_2 \in \mathcal{E}$, $E_1 \neq E_2$

$$|E_1 \cap E_2| \leq 2 \ . \qquad \square \tag{20}$$

Problem 64 ***(PhD 5.28.P.)*** *If* $|V| = m$, *what is the* minimal *value of*

$$s\,(m) := |\mathcal{S}_4| + |\mathcal{S}_5| \quad ? \qquad \square \tag{21}$$

Theorem 65 ***(PhD 5.30.T.)*** *Under Condition 63 and* $m \geq 58$ *we have a constant* $C_1 \leq 17$ *such that*

$$s\,(m) \geq \binom{m}{4} - \frac{1}{6} C_1 m^3 - \mathcal{O}\left(m^2\right) \ . \qquad \square \tag{22}$$

Further questions in matroids and hypergraphs

Problem 66 ***(PhD 5.33.P.)*** *Determine the minimal number of bases and circuits in matroids having neither loops nor parallel elements, and find the structures of the extremal ones.*

Definition 67 ***(PhD 5.34.D.)*** *The* ***girth*** *of a matroid is the length of his shortest circle.* □

Problem 68 ***(PhD 5.35.P.)*** *Determine the minimal number of bases and circuits in matroids having girth at least k .* □

Conjecture 69 ***(Oxley*** [O97], ***PhD 5.36.S.)*** *The uniform matroid $U_{m-3,k}$ has minimal number of circles if the girth is required to be at least k :*

$$1+3\cdot\binom{m-3}{k-1}+3\cdot\binom{m-3}{k-2}+\binom{m-3}{k-3}\leq simp(\mathcal{M})\ . \qquad \square \tag{23}$$

The generalization of Theorem 65 could be Problem 71 below.

Definition 70 ***(PhD 5.37.D.)*** *The edge $E\in\mathcal{E}_{k+1}$ is a* ***semi-simplex*** *if $E\not\supseteq F$ for $F\in\mathcal{E}_k$ $(k\in\mathbb{N})$. The* set *of the $k+1$-element semi-simplexes is*

$$\mathcal{E}^o_{k+1}\ . \qquad \square \tag{24}$$

Problem 71 ***(PhD 5.38.P.)*** *For any $m,k\in\mathbb{N}$ and $m=|V|$ find the mininal value of*

$$s_k\left(m\right):=\left|\mathcal{E}_k\right|+\left|\mathcal{E}^o_{k+1}\right|\ . \tag{25}$$

Conjecture 72 ***(PhD 5.39.S.)*** *Assuming (20) and $k\in\mathbb{N}$*

$$s_k\left(m\right)\geq\binom{m}{k}-\mathcal{O}\left(m^{k-1}\right)\ . \qquad \square \tag{26}$$

Further results will appear in [2013a].

Thesis V

Sharp upper bound was given for the number of circles and bases in matroids of given size and rank, moreover the structure of the extremal matroids was described (PhD 5.4.T. and 5.7.T.).

Sharp lower bound was given for the number of circles and bases in the case *loops are allowed* in matroids, the structure of the extremal matroids was described, too (PhD 5.8.T. and 5.9.T.).

Sharp lower bound was given for the number of circles and bases in the case *paralel elements are allowed but no loops* (PhD 5.13.T., 5.15.T., 5.21.T.).

A similar *general question* was formulated and solved *for hypergraphs* (PhD 5.24.T., 5.25.T. and 5.30.T.). ■

6. Hierarchy and valuating operator

Problems 10 and 11 follow. The mathematical definitions and theorems presented here are very simple but they have interesting meaning in chemistry ([2000b]).

Hierarchy

Species are linear combinations of atoms, reactions are linear combinations of species, go on to mechanisms, the inputs of the higher levels are exactly the outputs of the lower ones. Isomer molecules make the definition somewhat more complicated. Further details are planned to publish in [2013b].

Definition 73 ***(PhD 6.3.D.)*** *Let the sets* $\mathcal{A}_x = \left\{A_1^x, ..., A_{d_x}^x\right\}$ *be arbitrary for* $x \in \mathbb{N}$ *and consider the set of (formal) linear combinations* $L_x := \left\{\sum_{j=1}^{d_x} \alpha_j \cdot A_j^x : \alpha_j \in \mathbb{Z}\right\}$ *and the free modulus*

$$\mathcal{L}_x := (L_x, +, \cdot) \quad . \tag{27}$$

Any functions $\Delta_x^- : \mathcal{A}_x \to L_x$ $(x \in \mathbb{N} \setminus \{0\})$ *can be extended uniquely to homomorphisms*

$$\Delta_x : \mathcal{L}_x \to \mathcal{L}_{x-1} \quad , \tag{28}$$

we require further for $1 < x$

$$\Delta_{x-1} \circ \Delta_x = O \quad . \tag{29}$$

$\mathcal{L}_x$ *is the* x***-th stoichiometric level*** *and* Δ_x *are the the* ***connetctions****, (29) is called the generalized* ***law of mass balance.*** □

The evaluating operator

Definition 74 ***(PhD 6.5.D.) (i)*** *We call the elements of an arbitrary set* $\{C_1, \ldots, C_n\}$ ***components****, the linear combination* $\underline{S} = \sum_{i=1}^n s_i \cdot C_i$ $(s_i \in \mathbb{R})$ *are (chemical)* ***structures****, the sets* $V := \{\sum_{i=1}^n s_i \cdot C_i : s_i \in \mathbb{R}\}$ *are* ***sets of massess****.*
(ii) *Any linear functional* $\mathcal{L} : V \to \mathbb{R}$ *is called* ***evaluating operator****.* □

Theorem 75 ***(PhD 6.6.T.)*** *All the evaluating operators on* V *have the form*

$$\mathcal{L}(\underline{S}) = \sum_{i=1}^n a_i \cdot s_i \tag{30}$$

where the coefficient vector $\underline{a} = [a_1, \ldots, a_n]^T \in \mathbb{R}^n$ *is uniquely determined by* $\mathcal{L} : a_i = \mathcal{L}(C_i)$. □

Immediately we get the proof of Hess' theorem:

Theorem 76 ***(PhD 6.7.T.,*** Hess' law***)*** *If the reactions* $X_1, \ldots, X_k$ *result the zero mechanism* $\underline{\mathcal{O}}$ *then the sum of the heats* $\mathcal{H}(X_1), ..., \mathcal{H}(X_k)$ *is* 0. □

The fact $V^* \cong V$ implies

Theorem 77 ***(PhD 6.8.T.)*** *If* V *is built up from* n *components, then there are* at most n *linearly independent evaluating operators* $\mathcal{L}_1, ..., \mathcal{L}_n$ *, so all each other evaluating operator* $\mathcal{L}$ *can be expressed as* $\mathcal{L} = \alpha_1\mathcal{L}_1 + ... + \alpha_n\mathcal{L}_n$. □

Using Cauchy-Bunyakowsky-Schwarz's inequality:

Theorem 78 ***(PhD 6.9.T.)*** *For any* V *and* $\mathcal{L} : V \to \mathbb{R}$ *there is a constant* $c \in \mathbb{R}^+$ *such that*

$$| \mathcal{L}(\underline{S}) | \leq c \cdot \|\underline{S}\| \quad \text{for } \underline{S} \in V \ , \tag{31}$$

where $\|\underline{S}\| = \sqrt{s_1^2 + \ldots + s_n^2}$, $c = \sqrt{a_1^2 + \ldots + a_n^2}$, s_i *and* a_i *are defined in Definitions 73 and 75.* □

Theorem 79 ***(PhD 6.10.T.)*** *If* V_1 *and* V_2 *are generated by* $\mathcal{C} = \{C_1, \ldots, C_n\}$ *and* $\mathcal{D} = \{D_1, \ldots, D_m\}$ *resp,,* $\mathcal{C} \cap \mathcal{D} = \emptyset$ *and* $V = V_1 \oplus V_2$ *, then* V *has evaluating operators*

$$\mathcal{L} = \mathcal{L}\,|_{V_1} \oplus \mathcal{L}\,|_{V_2} \tag{32}$$

only: $\mathcal{L}(\underline{S}) = \sum_{i=1}^n a_i s_i + \sum_{j=1}^m b_j t_j$ *for* $\underline{S} = \sum_{i=1}^n s_i C_i + \sum_{j=1}^m t_j D_j$. □

Theorem 80 ***(PhD 6.11.T.)*** *For any two scalar products* $\mathcal{A}, \mathcal{B} : V \times V \to \mathbb{R}$ *there is an* continuous *automorphism* $\mathcal{I} : V \to V$ *such that* $\mathcal{A}(\underline{u}, \underline{v}) = \mathcal{B}(\mathcal{I}(\underline{u}), \mathcal{I}(\underline{v}))$ $(\underline{u}, \underline{v} \in V)$. □

Roughly speaking this means, that all the evaluating operators of a mass-set differ from a scalar multiplier only.

Thesis VI

i) A *general definition of stoichiometric hierarchy* was given (PhD 6.3.D.)
ii) The general notion of *valuation operator* was stated. We used this notion to give *chemical meanings* for several (wellknown) theorems in linear algebra, so we obtained both *short mathematical proof* for Hess' law and also formulated *new Statements* in chemistry (PhD 6.5.D., 6.6.T.-6.11.T.). ■

7. Examples

"Amundson" ([A66], [P90])

We are given the species:
$CO, CO_2, O_2, H_2, CH_2O, CH_3OH, C_2H_5OH, (CH_3)_2CO, CH_4, CH_3CHO, H_2O$
The 213 simplexes were found in 0.22 seconds. The output starts as :

$-2CO + 2CO_2 - O_2 = 0$,
$3CO - CO_2 + 3H_2 - C_2H_5OH = 0$,
$5CO - 2CO_2 + 3H_2 - C_2H_6CO = 0$,
$2CO - CO_2 + 2H_2 - CH_4 = 0$,
$3CO - CO_2 + 2H_2 - CH_3CHO = 0$,
$-1CO + CO_2 + H_2 - H_2O = 0$, **...** .

"Methane" ([B99], [HS83])

Synthetizing methane from carbonmonoxide and water. We have to build the overall reaction $\mathbf{S}_R$ from $S_1 - S_{15}$ (ℓ is the catalisator)

$\mathbf{S}_R$: $\mathbf{2H_2 + 2CO \rightarrow CH_4 + CO_2}$,
$S_1 : CO\ell + \ell = C\ell + O\ell$,
$S_2 : C\ell + H\ell = CH\ell + \ell$,
$S_3 : CH\ell + H\ell = CH_2\ell + \ell$,
$S_4 : CH_2\ell + H\ell = CH_3\ell + \ell$,
$S_5 : CH_3\ell + H\ell = CH_4 + 2\ell$,
$S_6 : OH\ell + H\ell = H_2O + 2\ell$,
$S_7 : CO_2 + \ell = CO_2\ell$,
$S_8 : CO + \ell = CO\ell$,
$S_9 : H_2 + 2\ell = 2H\ell$,
$S_{10} : CO_2\ell + H\ell = CHOO\ell + \ell$,
$S_{11} : CHOO\ell + H\ell = CHO\ell + OH\ell$,
$S_{12} : O\ell + H\ell = OH\ell + \ell$,
$S_{13} : CO\ell + O\ell = CO_2\ell + \ell$,
$S_{14} : CHOO\ell + \ell = OH\ell + CO\ell$,
$S_{15} : CO\ell + H\ell = CHO\ell + \ell$.

The minimal mechanisms (output), the latest three are cycles only:

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) $S_{11} - S_{14} - S_{15} = 0$

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