

## NEW DISCOVERED PARADOXES IN THEORY OF BALANCING CHEMICAL REACTIONS

### NOVOODKRITI PARADOKSI V TEORIJI URAVNOTEŽENJA KEMIJSKIH REAKCIJ

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»Failure to distinguish carefully between *mathematical*  
and *metamathematical* statements leads to paradoxes.«

M. Kac, S. M. Ulam, *Mathematics and Logic*,  
Dover Pub. Inc., Mineola 1992, p. 126.

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In this work are given new paradoxes and fallacies discovered in the theory of balancing chemical reactions. All the counterexamples showed that so-called »*chemical procedures*« of balancing chemical reactions given in earlier chemical literature are inconsistent. Balancing chemical reactions is a mathematical procedure independent of chemistry. In order to avoid the appearance of paradoxes, chemical reactions must be considered as a formal system founded by virtue of well-defined mathematical model. The results obtained in this work affirmed that the usage of traditional ways of balancing chemical reactions is limited. They may be used only for balancing some elementary chemical equations. In other words, foundation of chemistry looks for a new approach of balancing chemical reactions, which must be completely different than current »*chemical procedures*«. This work is a collection and analysis of some paradoxes and fallacies which appeared in the theory of balancing chemical reactions.

Keywords: chemical reactions, paradoxes, balancing, fallacies

Predstavljeni so novi paradoksi in zmote, odkrite v teoriji uravnoteženja kemijskih reakcij. Vsi protiprimeri so pokazali, da so tako nekonsistentne tako imenovane kemijske procedure uravnoteženja kemijskih reakcij, navedene v zgodnjih virih. Uravnoteženje kemijskih reakcij je matematična procedura, neodvisna od kemije. Da bi se izognili nastajanju paradoksov, je treba kemijske reakcije formulirati kot formalen sistem na podlagi dobro definirane matematičnega modela. Rezultati v tem delu potrjujejo, da je uporaba tradicionalnih načinov uravnoteženja kemijskih reakcij omejena. Uporabljamo jo le za uravnoteženje nekaterih elementarnih kemijskih reakcij. Z drugih besedami, temelj kemije išče nove približke za uravnoteženje kemijskih reakcij, ki se morajo razlikovati od sedanjih kemijskih procedur. To delo je izbor in analiza nekaterih paradoksov in zmote, ki so se pojavile v teoriji uravnoteženja kemijskih reakcij.

Ključne besede: kemijske reakcije, paradoksi, uravnoteženje, zmote

## 1 INTRODUCTION

In this section we shall discuss the balancing of chemical reactions from scientific viewpoint. It is an essential precondition for better understanding of our discourse about paradoxes connected with traditional ways of balancing chemical reactions.

Before opening this discussion about balancing chemical reactions, we would like to give a few remarks about the name of so-called course »*general chemistry*«. Why? The reply is very simple, because this course treats the balancing of chemical reactions as its subject. At the beginning of our exposition we want to say that the name »*general chemistry*« is not appropriately chosen. Generally speaking, »*general chemistry*« does not exist, and on top of all it is not possible to exist, because the principles of this particular chemistry are weak and do not hold for all parts of chemistry. They have only particular meaning and nothing more. In other words, it means that its principles are not general. This is just one thing. Another thing, chemistry is founded by virtue of

mathematical principles, but also there not exists »*general mathematics*« and speaking more accurately it is not possible to exist.

For instance, in *mathematical logic* in the 20<sup>th</sup> century lots of paradoxes were discovered,<sup>1</sup> and mathematicians thought that only there are possible antinomies and that other parts of mathematics are in safety. Reality showed that it is not true. In *mathematical analysis* lots of counterexamples were found.<sup>2,3</sup> Also certain counterexamples were found in *probability & statistics*.<sup>3</sup> <sup>4</sup> In *topology* as a contemporary mathematical discipline a great number of counterexamples were detected too.<sup>5</sup> It does not mean that other mathematical disciplines are without contradictions. No! Just the opposite, in almost all the branches of mathematics different kinds of counterexamples are detected<sup>6</sup>. These facts show that mathematical principles are not general, *i. e.*, they hold only in certain part of mathematics. These are the causes why there is not »*general mathematics*«. If we take into account the fact that chemical reaction is a basic issue in chemistry and according to its definition (see: Definition

2.2, in the section 2), then it follows that chemistry is founded on mathematical principles. If there is not »*general mathematics*«, then how is possible to exist »*general chemistry*«? Simply speaking, it is impossible!

In order to correct this irrational name of chemistry, it is necessary to choose an appropriate name which will be more suitable for that particular chemistry. For example, the names *basic chemistry* and *elementary chemistry* fit for that chemistry.

In chemical as well as mathematical journals there are lots of published papers which treat the problem of balancing chemical reactions. Specially, in chemical journals are considered many different so-called »*chemical ways*« for balancing chemical reactions, but unfortunately all of them offer only particular procedures for balancing of some simple chemical reactions. These »*chemical ways*« very often have negative consequences for chemistry. For instance, they produce fallacies or absurd results, because most of them work on *erroneous principles*, but not on true principles.

Balancing chemical reactions is not a simple procedure as some traditionally oriented chemists think or as they want to be. In<sup>7</sup> the author emphasized very clearly, that *balancing chemical reactions is not chemistry; it is just linear algebra*.

Balancing chemical reactions is a basic matter of chemistry, if not one of its most important issues, and it plays a main role in its foundation. Indeed, it is a subtle question, which deserves considerable attention.

This topic has always excited nature as deeply as no other question in chemistry. The balancing of chemical reactions has acted upon human mind in such stimulating and fruitful way as hardly any other idea, but also this subject needs an explanation as no other concept.

The concept of *balancing chemical reactions* in chemistry is tracked and transformed from traditionalism to intuitionism in the 19<sup>th</sup> century, from intuitionism to irrationalism in the first half of 20<sup>th</sup> century, from irrationalism to particularism in the second half of 20<sup>th</sup> century, while the particularism is sharpened by Moore–Penrose matrix<sup>8, 9</sup> concept into generalism and transformed into formalism, which takes on the status of a paradigm in the 21<sup>st</sup> century.

To the question of balancing chemical reactions the mathematicians, chemists and computer engineers with different conceptions will not always give the same answer. A mathematician, a chemist and a computer engineer will answer each in a different way. Some of them will admit that perhaps the others are right in a *certain sense* and will try to *reinterpret* the others' procedures in their own language. But in general everyone, more or less, will remain convinced that, in fact, still only he is right.

Since chemistry is not immune from contradictions, also we found several absurd results there when balancing chemical reactions. In this work only just these absurd contradictions are studied.

Sometimes the mistakes in reasoning come because our experience with one situation causes us to assume that the same reasoning will hold true in a related but different situation. This kind of mistake can occur at a very simple level or at a more complex one. At a simple level, the most common conclusion is that we know that we have to reject the reasoning, although it may be difficult to say why. At the more complex level, we may conclude that the reasoning must be accepted even when the results seem to contradict our notion of how the real world works.

Scientific research and experience have shown, when the results of reasoning and mathematics conflict with experience, then there is probably a *fallacy* of some sort involved<sup>10</sup>.

In the literature<sup>11–13</sup> there are a great number of definitions for fallacy, but we shall mention merely few of them. For us is important only *deductive fallacy*. A *deductive fallacy* is a deductive reason that is illogical.

In philosophy, the term *logical fallacy* suitably refers to a *formal fallacy*. It is defined as *a defect in the structure of deductive reason, which makes the reason invalid*. Most textbooks echo the *standard treatment* of fallacy, as a reason, which *seems to be valid but is not so*<sup>14</sup>. According to Maxwell<sup>15</sup>, a fallacy *leads by guile to a wrong but plausible conclusion*.

In mathematics the word *fallacy* could also refer to a truthful result obtained by wrong reasoning.

In looking at wrong thinking about easy ideas, we found some cases in which reasoning about balancing chemical equations is wrong.

As long as we cannot recognize what the *fallacy* is, the situation is a *paradox*. In some cases, as we shall see, the paradox is entirely inside chemistry. For most paradoxes that are inside chemistry, elimination of the fallacious reasoning produces a *purified* chemistry that is a better description of the real chemistry than the *contaminated* chemistry was.

In philosophy there is a bunch of different definitions of paradoxes.

According to Sainsbury,<sup>16</sup> *a paradox is an apparently unacceptable conclusion derived by apparently acceptable reasoning from apparently acceptable premises*. Rescher<sup>17</sup> defines a paradox as *a set of propositions that are individually plausible but collectively inconsistent*. Chihara<sup>18</sup> provides a similar definition: *a paradox is an argument that begins with premises that appear to be clearly true, that proceeds according to inference rules that appear to be valid, but ends in contradiction*. Quine<sup>19</sup>, for example, offers the following definition (using the term *antinomy*, instead of a paradox): *An antinomy produces a self-contradiction by accepted ways of reasoning. It establishes that some tacit and trusted pattern of reasoning must be made explicit and hence-forward be avoided or revised*. In similar spirit, Koons<sup>20</sup> defines paradox as *an inconsistency among nearly nonrevisable principles that can be resolved only*

by recognizing some essential limitation of thought or language.

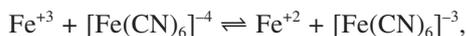
In the next section we shall consider the paradoxes which appeared in different parts of chemistry.

## 2 PRELIMINARIES

The word *paradox* in professional works has almost the same meaning as the word *contradiction*. Chemistry as other natural sciences is not immune of paradoxes. Unlike other natural sciences, in chemistry paradoxes appeared some time later, and it has some of them, while other sciences are overfull of such contradictions.

Now, we shall mention the well-known paradoxes in chemistry. They are:

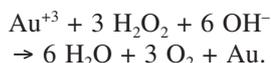
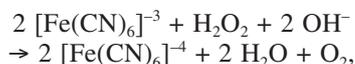
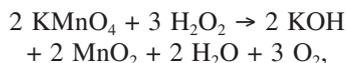
□ The Prussian blue paradox:<sup>21</sup> *The reaction between ferric and ferrocyanide ions to form Prussian blue and ferrous and ferricyanide ions to form Turnbull's blue are profoundly influenced by the occurrence of the ionic redox equilibrium:*



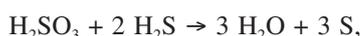
which is largely displaced toward the right.

□ Feigl's paradoxes:<sup>22</sup>

- Hydrogen peroxide as a reducing agent (Oxidizing agents undergo mutual reduction)



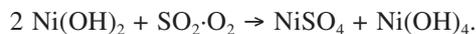
- Sulfurous acid brings about oxidations



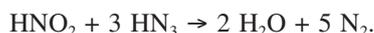
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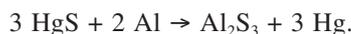
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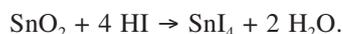
- Nitric acid is not an oxidant



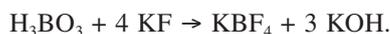
- Oxidation of aluminum at room temperature



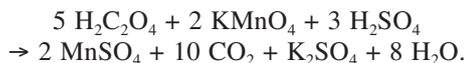
- Nonvolatile oxides of tin and antimony are made to disappear by heating them with a volatile compound



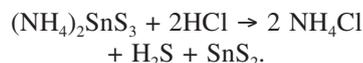
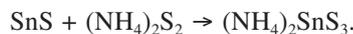
- An acid sets a base free from a salt



- Permanganate is not capable of oxidizing oxalic acid



- Ammonium polysulfide brings about an oxidation



□ Levinthal's paradox:<sup>23</sup> *The length of time in which a protein chain finds its folded state is many orders of magnitude shorter than it would be if it freely searched all possible configurations.*

□ Quantum chemistry paradoxes:<sup>24</sup>

- Preponderant configurations.
- Relevant symmetry.
- Watson effect.
- High ionization energies of the partly filled shells.
- Continua of penultimate ionization.
- Continua of translational energy.
- Questions of time-scale.
- Quantum mechanics pretends to be valid for other systems than electrons.
- Assembly properties and repeated small entities.
- Campbell's paradoxes:<sup>25</sup>
- A catalyst is a substance which increases the rate of a reaction without entering into it.
- System tends to a minimum in potential energy.
- The entropy of a shuffled deck of cards is greater than that of a new deck.
- Energy is the ability to do work.

□ Paradoxes of spin-pairing energy in gadolinium (III)<sup>26</sup>: *The spin-pairing parameter  $D = 9E^1/8$  for  $4f^q$  separates the averages of all states ( $S_0$ ) and ( $S_{0-1}$ ) to the extent  $2DS_0$  where  $Gd^{+3}$  has  $D = 0.80$  eV. Hartree-Fock (flexible radial functions) have previously been performed for each of the four  $S$ , producing a value of  $D = 1.09$  eV but the contributions to  $D$  from kinetic energy  $T$ , electron-nuclear attraction  $Q$ , and interelectronic repulsion  $C$  with ratios  $-1.6:(-4)$  distributed  $T_c$  (3.5),  $T_f$  (-4.5),  $Q_c$  (-7),  $Q_f$  (13),  $C_{cc}$  (3.5),  $C_{cf}$  (-7.9),  $C_{ff}$  (0.4) indexed  $c$  (closed nl shells) and  $f$  (4f). Pragmatic  $D = 0.80$  eV corresponds to 1.84 times the calculated contribution from  $C_{ff}$  and to  $-0.184$  times the sum of  $C$  integrals. Additional complications are expected from the correlation energy  $-100$  eV.*

□ Structure-Activity Relationship (SAR) paradox<sup>27</sup>: *Exceptions to the principle that a small change in a molecule causes a small change in its chemical behavior are frequently profound.*

□ Helium paradoxes:<sup>28</sup> *The relatively high  $^4\text{He}/^{21}\text{Ne}$ ,  $^3\text{He}/^{22}\text{Ne}$  and  $^4\text{He}/\text{CO}_2$  ratios in midocean ridge basalts suggest that it is the midocean ridge basalt reservoir that is He-rich and that the high ratio  $^3\text{He}/^4\text{He}$  in midocean ridge basalts is due to excess  $^4\text{He}$ , not a deficit in the 'primordial' isotope  $^3\text{He}$ .*

□ Temperature dependence of  $\Delta G^\circ$  and the equilibrium constant  $K_{eq}$ .<sup>29</sup> The sign of  $\Delta S^\circ$  determines the temperature dependence of  $\Delta G^\circ$ , it is  $\Delta H^\circ$  that is responsible for the shift in  $K_{eq}$  with temperature.

□ The  $q/T$  paradox:<sup>30</sup> Which ‘contains more heat’, a cup of coffee at 95 °C or a liter of icewater?

□ pH paradox:<sup>31</sup>  $pH \equiv -\lg[H^+]$ .

□ Parrondo’s paradox<sup>32</sup>: A mathematical concept known as Parrondo’s paradox is the unexpected situation in which two specific losing strategies can, by alternating between them, produce a winning outcome.

□ Parrondo’s paradox motivated the development of many new computational models of chemical systems, in which thermal cycling problem is studied.<sup>33</sup> By these kinetics systems compare the rates of formation of products under temperature-cycling and steady-state conditions. Also, these computational models of thermal cycling announce new applications in chemistry, biochemistry and chemical engineering. More essentially, by these models one obtains knowledge that some simple chemical systems might behave paradoxically, and that forced oscillating conditions may induce an outcome.

However, these paradoxes are not alone and there are more which appears in the theory of balancing of chemical equations. Just these paradoxes are main research object in this work.

### 3 A NEW CHEMICAL FORMAL SYSTEM

Chemists must introduce a whole set of auxiliary definitions to make the chemistry work consistently. The more abstract the theory is, the stronger the cognitive power is.

What does it mean a chemical equation? The reply of this question lies in the following descriptive definition given in a compact form.

**Definition 2.1.** Chemical equation is a numerical quantification of a chemical reaction.

Let  $\mathcal{X}$  be a finite set of molecules.

**Definition 2.2.** A chemical reaction on  $\mathcal{X}$  is a pair of formal linear combinations of elements of  $\mathcal{X}$ , such that

$$\rho: \sum_{j=1}^r a_{ij} x_j \rightarrow \sum_{j=1}^s b_{ij} y_j \quad (1 \leq i \leq m) \quad (2.1)$$

with  $a_{ij}, b_{ij} \geq 0$ .

The coefficients  $x_j, y_j$  satisfy three basic principles (corresponding to a closed input–output static model)

- the law of conservation of atoms,
- the law of conservation of mass, and
- the reaction time–independence.

**Definition 2.3.** Each chemical reaction  $\rho$  has a domain

$$\text{Domp} = \{x \in \mathcal{X} \mid a_{ij} > 0\} \quad (2.2)$$

**Definition 2.4.** Each chemical reaction  $\rho$  has an image

$$\text{Imp} = \{y \in \mathcal{X} \mid b_{ij} > 0\} \quad (2.3)$$

**Definition 2.5.** Chemical reaction  $\rho$  is generated for some  $x \in \mathcal{X}$ , if both  $a_{ij} > 0$  and  $b_{ij} > 0$ .

**Definition 2.6.** For the case as the previous definition, we say  $x$  is a generator of  $\rho$ .

**Definition 2.7.** The set of generators of  $\rho$  is thus  $\text{Domp} \cap \text{Imp}$ .

Often chemical reactions are modeled like pairs of multisets, corresponding to integer stoichiometric constants.

**Definition 2.8.** A stoichiometrical space is a pair  $(\mathcal{X}, \mathcal{R})$ , where  $\mathcal{R}$  is a set of chemical reactions on  $\mathcal{X}$ . It may be symbolized by an arc-weighted bipartite directed graph  $\Gamma(\mathcal{X}, \mathcal{R})$  with vertex set  $\mathcal{X} \cup \mathcal{R}$ , arcs  $x \rightarrow \rho$  with weight  $a_{ij}$  if  $a_{ij} > 0$ , and arcs  $\rho \rightarrow y$  with weight  $b_{ij}$  if  $b_{ij} > 0$ .

Let us now consider an arbitrary subset  $\mathcal{A} \subseteq \mathcal{X}$ .

**Definition 2.9.** A chemical reaction  $\rho$  may take place in a reaction combination composed of the molecules in  $\mathcal{A}$  if and only if  $\text{Domp} \subseteq \mathcal{A}$ .

**Definition 2.10.** The collection of all feasible reactions in the stoichiometrical space  $(\mathcal{X}, \mathcal{R})$ , that can start from  $\mathcal{A}$  is given by

$$\mathcal{R}_A = \{\rho \in \mathcal{R} \mid \text{Domp} \subseteq \mathcal{A}\}. \quad (2.4)$$

In<sup>34</sup> is proved the following proposition.

**Proposition 2.11.** Any chemical equation may be presented in this form

$$\sum_{j=1}^r x_j \prod_{i=1}^m \Psi_{a_{ij}}^i = \sum_{j=1}^s y_j \prod_{i=1}^m \Omega_{b_{ij}}^i \quad (2.5)$$

where  $x_j$  ( $1 \leq j \leq r$ ) and  $y_j$  ( $1 \leq j \leq s$ ) are unknown rational coefficients,  $\Psi^i$  and  $\Omega^i$  ( $1 \leq i \leq m$ ) are chemical elements in reactants and products, respectively,  $a_{ij}$  ( $1 \leq i \leq m; 1 \leq j \leq r$ ) and  $b_{ij}$  ( $1 \leq i \leq m; 1 \leq j \leq s$ ) are numbers of atoms of elements  $\Psi^i$  and  $\Omega^i$ , respectively, in  $j$ -th molecule.

**Definition 2.12.** The nullity of the reaction matrix  $A$  is

$$\text{nullity}A = n - r, \quad (2.6)$$

where  $n$  is the total number of reaction molecules and by  $r = \text{rank}A$  the rank of the matrix  $A$  is denoted.

**Definition 2.13.** For any chemical reaction these criteria hold:

- 1° if  $\text{nullity}A = 0$ , then the reaction is unfeasible,
- 2° if  $\text{nullity}A = 1$ , then the reaction is unique, and
- 3° if  $\text{nullity}A > 1$ , then the reaction is non-unique.

We shall define a fallacy in this way.

**Definition 2.14.** A wrong result attached with a seemingly logical explanation of why the result is correct is a fallacy.

A new definition for a paradox should look like this.

**Definition 2.15.** A paradox is a seemingly true assertion that leads to an inconsistency or a situation, which resists intuition.

What does it mean the term non-stoichiometric? Briefly, it means that a substance may participate in two different reactions simultaneously, in which case the relative amounts of two products would bear no fixed ratio to one another.

According to this, now we can define a non-stoichiometric reaction as a real vector space.

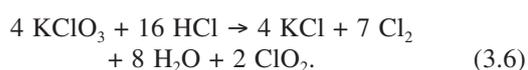
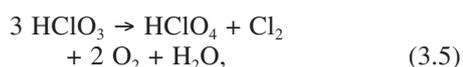
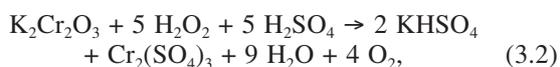
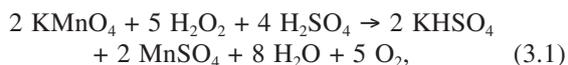
**Definition 2.16.** *A non-stoichiometric reaction is a vector space in which a given set of vector-molecules as reactants gives final vector-molecules as products whose molecular proportions are variable in a continuous sense.*

#### 4 NEW PARADOXES AND FALLACIES

In this section we shall present chronologically the new paradoxes and fallacies, which we discovered in the theory of balancing chemical reactions.

I. Steinbach gave this statement<sup>35</sup>: *While chemical equations may balance algebraically, they are not necessarily stoichiometrically exact.*

In order to illustrate the above statement, »as the correct stoichiometric equations«, he »balanced« the following chemical reactions



He said: *Obviously there are an infinite number of solutions for the coefficients. Only a few of the total possible solutions are given.*

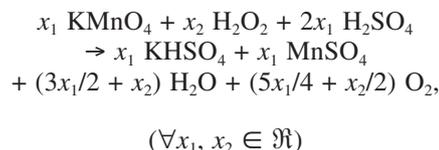
Next, he stated: *when equations are balanced by either the valence-change or the ion-electron methods, the coefficients obtained are the correct stoichiometric ones.*

He finished his article like this: *Equations (3.1) ÷ (3.6) have no stoichiometric meaning, and it is doubtful whether they have any real significance other than that they contain the short-hand suggestion of the reactants used and the products obtained. They do, however, have a definite suggestion that further investigation would be most desirable. It is by examples such as these that the wide divergence between the stoichiometric equation and the actual mechanism of a chemical reaction is so poignantly revealed.*

All the statements mentioned above are *paradoxical*. Why these statements are inconsistent will be explained in the following text.

Now, we shall make a very clean distinction what is what! The first statement is completely wrong, because the algebraic method has not any restriction of its usage. It holds for every chemical reaction, while other so-called »chemical methods« hold only for some particular cases.

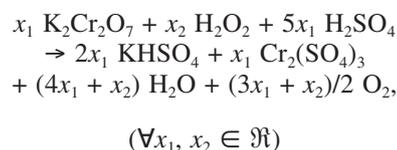
From the general solution of the reaction (3.1),



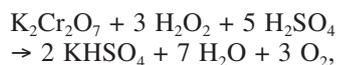
we can see that it is a correct two-parametric stoichiometric reaction, but not as stated Steinbach. It is just one thing. Another thing, he »offered« only a particular solution of (3.1) for  $x_1 = 2$  and  $x_2 = 5$ . Immediately, after publication of his article<sup>35</sup>, Hall<sup>36</sup> pointed out, the statement for the reaction (3.1) that is a »good« example of variable coefficients is absolutely wrong. It has been known to be stoichiometric for many, many years and was studied by C. F. Schönbein, who found that particular reaction as expressed by (3.1).

**Remark 3.1.** *Schönbein's particular solution is obtained under certain experimental conditions and it does not mean that for other different condition other solutions will not be possible!*

Chemical reaction (3.2) is balanced incorrectly! The coefficients of the above reaction correspond to this chemical reaction

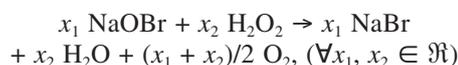


for  $x_1 = 1$  and  $x_2 = 5$ . The reaction that is offered by Hall<sup>36</sup>



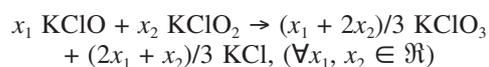
is balanced wrongly too!

The general solution of the reaction (3.3) is



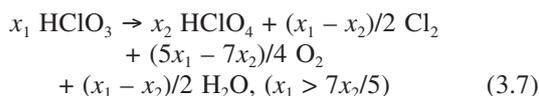
and Steinbach found a particular solution for  $x_1 = x_2 = 1$ . Again, we had not any limitations with the usage of the algebraically method. Also, in this case the method worked perfectly.

Chemical reaction (3.4) has this general solution



and the above particular solution corresponds for  $x_1 = x_2 = 1$ .

The general solution of the chemical reaction (3.5) is



For  $x_1 = 3$  and  $x_2 = 1$ , as a particular case from (3.7) immediately follows (3.5).

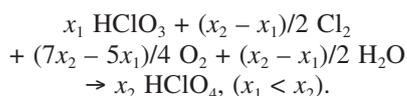
For  $x_1 = x_2$ , from (3.7) one obtains this elementary reaction



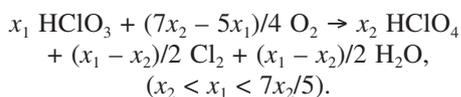
For  $x_1 = 7x_2/5$ , chemical reaction (3.7) transforms into



If  $x_1 < x_2$ , then (3.7) becomes

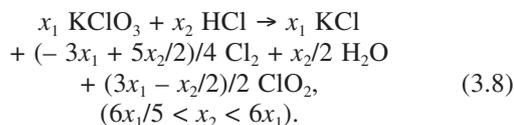


If  $x_2 < x_1 < 7x_2/5$ , then chemical reaction (3.7) attains this form



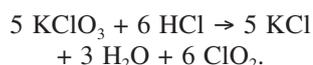
For the reactions (3.3), (3.4) and (3.5) Lehrman<sup>37</sup> with the mentioned particular cases gave a comprehensive construction of *ad infinitum* equations.

The last reaction (3.6), between potassium chlorate and hydrochloric acid, has a general solution



For  $x_1 = 4$  and  $x_2 = 16$  from the chemical reaction (3.8) as a particular solution follows (3.6).

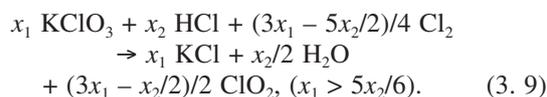
For  $x_1 = 5x_2/6$ , from (3.8) one obtains this elementary reaction



For  $x_1 = x_2/6$ , then (3.8) becomes



If  $x_1 > 5x_2/6$ , then (3.8) transforms into



We would like to emphasize here that all the reactions are balanced by the well-known algebraically method, and all the two-parametric coefficients are correct. It is completely different from the third Steinbach's statement given above, which gives advantage to the valence-change or the ion-electron methods.

If we take into account the very well-known rule that equations for consecutive reactions may be added and equations for concurrent reactions may not be added, then obviously Steinbach brings up the old, very old er-

ror involved in adding equations for concurrent reactions. It is his biggest mistake.

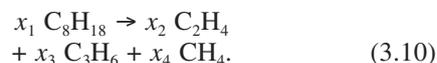
What happens when the reactions are not unique according to Steinbach? In that case, he »*balanced*« them as an infinite number of reactions, which do not express actual stoichiometric relations. They are »*derived*« by combining together the reactions for concurrent reactions, in which coefficients in each of the two or more reactions are previously multiplied by different numbers. Sure, these reactions are incorrect, as they do not correspond to the real stoichiometric relations among the substances, which are involved. In some cases, there is no constant relation among the quantities of substances expressed by his reactions. The ratio of the quantities will depend upon chemical conditions (concentration, temperature, etc.).

The above Steinbach's reactions, in fact, are oxidation-reduction reactions for which we found the general solutions by using of algebraic method. Every one of them in fact represents two chemical reactions, not one as Steinbach stated. Therefore, these reactions are not *non-stoichiometric reaction!* Standen in his article<sup>38</sup> named these Steinbach's reactions as *bizarre non-stoichiometric equations*.

McGavock in<sup>39</sup> gave a note on errata in the Steinbach's article<sup>35</sup>.

In order to explain what a *non-stoichiometric reaction* represents, McGavock considered an example from his book<sup>40</sup>.

**Example 3.2.** It is the cracking reaction



Now, we shall show that the above reaction (3.10) is not a *non-stoichiometric* reaction.

From the scheme given below

	$\nu_1 = \text{C}_8\text{H}_{18}$	$\nu_2 = \text{C}_2\text{H}_4$	$\nu_3 = \text{C}_3\text{H}_6$	$\nu_4 = \text{CH}_4$
C	8	2	3	1
H	18	4	6	4

follows this vector equation

$$x_1 \nu_1 = x_2 \nu_2 + x_3 \nu_3 + x_4 \nu_4,$$

*i. e.*,

$$x_1 (8, 18)^T = x_2 (2, 4)^T + x_3 (3, 6)^T + x_4 (1, 4)^T,$$

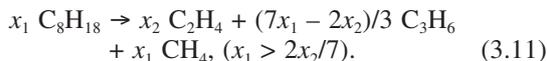
or

$$(8x_1, 18x_1)^T = (2x_2 + 3x_3 + x_4, 4x_2 + 6x_3 + 4x_4)^T.$$

From the system of linear equations

$$\begin{aligned} 8x_1 &= 2x_2 + 3x_3 + x_4, \\ 18x_1 &= 4x_2 + 6x_3 + 4x_4, \end{aligned}$$

one obtains  $x_4 = x_1$  and  $x_3 = (7x_1 - 2x_2)/3$ . Now, balanced chemical equation has this general solution



The vectors  $\mathbf{v}_1$ ,  $\mathbf{v}_2$ ,  $\mathbf{v}_3$  and  $\mathbf{v}_4$  of the molecules of the above chemical reaction are linearly dependent and they generate an infinite number of vector spaces  $V_\infty$  over  $\mathfrak{R}$ , *i. e.*, one obtains an infinite number of solutions  $[x_1, x_2, (7x_1 - 2x_2)/3, x_1]$ ,  $(x_1 > 2x_2/7)$ , that means that the chemical reaction (3. 10) is non-unique.

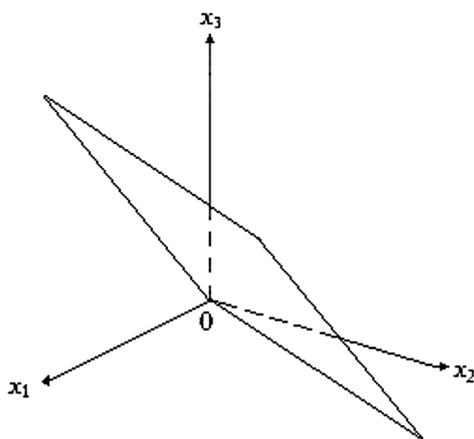


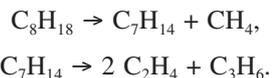
Figure 1: Plane  $7x_1 - 2x_2 - 3x_3 = 0$  in  $\mathfrak{R}^3$

However, it is not possible, either on an algebraic or empirical basis, to exclude nonintegral values for the coefficients. Each point of the plane  $7x_1 - 2x_2 - 3x_3 = 0$ , given on the **Figure 1**, represents a triad of positive, nonintegral values. Infinity of such points corresponding to infinity of triads of coefficients in the above equation exists. By virtue of this finding, it is asserted that this cracking reaction does not represent a *non-stoichiometric* reaction. It contradicts McGavock's statement.

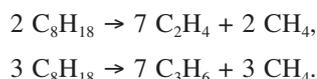
McGavock in<sup>39</sup> obtained this reaction



Actually, the reaction (3.12) is a particular solution of (3.11), for  $x_1 = 1$  and  $x_2 = 2$ . The above McGavock's »*non-stoichiometric*« reaction (3.12) according to Standen<sup>38</sup> can also be written as two reactions:



Before the reaction (3.12) be regarded as a genuine *non-stoichiometric* reaction, it must be shown that it is one reaction. It might be a combination of these two reactions:



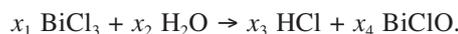
Also, this Standen's counterexample shows that chemical reaction (3.12) is not *non-stoichiometric* reaction.

By this and the Definition 2.16, we proved that McGavock's presentation for *non-stoichiometric reaction* is an ordinary fallacy.

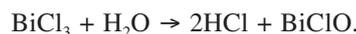
**II.** Porges in his article<sup>41</sup> wrote: *After examining a great many chemical equations, one concludes that most of them are of the type in which the number of compounds involved exceeds the number of elements by unity.*

This Porges' statement does not represent any criterion for balancing chemical equation and it is completely wrong. In fact, it is only an ordinary *paradox*! The counterexamples given below show it.

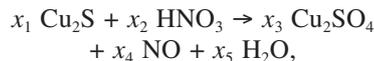
**Example 3.3.** Let us consider this elementary chemical reaction



Here, we have a case when the number of involved compounds does not exceed the number of elements by unity, *i. e.*, in this case four elements are involved in four molecules. The above chemical reaction reduces to a system of four linear equations in four unknown variables and the chemical reaction has a unique solution. The balanced reaction has this form

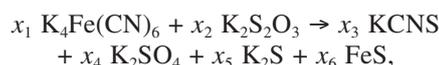


**Example 3.4.** For instance, in the chemical reaction



five elements are involved in five molecules. The above reaction has a unique solution  $x_1 = 3$ ,  $x_2 = 8$ ,  $x_3 = 3$ ,  $x_4 = 8$ ,  $x_5 = 4$ .

**Example 3.5.** In this particular reaction



are involved six elements and same number of molecules, *i. e.*, we have six linear equations in six unknown variables. The chemical reaction has a unique solution  $x_1 = 2$ ,  $x_2 = 12$ ,  $x_3 = 12$ ,  $x_4 = 9$ ,  $x_5 = 1$ ,  $x_6 = 2$ .

**Example 3.6.** The chemical reaction

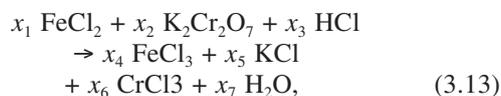


contains nine elements in five molecules and it reduces to a system of nine linear equations in five unknown variables. The chemical reaction has a unique solution  $x_1 = x_2 = \dots = x_5 = 1$ .

The mentioned four counterexamples contradict to the above Porges' statement. By this, we refuted his statement.

In the same article<sup>41</sup> there are *fallacies* too.

For instance, he reduced the chemical reaction



to the following system of linear equations

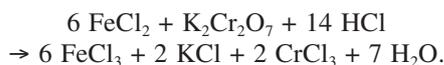
$$\begin{aligned}x_1 &= x_4, 2x_1 + x_3 = 3x_4 + x_5 + 3x_6, \\2x_2 &= x_5, 2x_2 = x_6, \\7x_2 &= x_7, x_3 = 2x_7.\end{aligned}\quad (3.14)$$

Immediately from (3.14), he obtained

$$\begin{aligned}x_1 &= 6x_2, x_2 = x_2, x_3 = 14x_2, x_4 = 6x_2, \\x_5 &= 2x_2, x_6 = 2x_2, x_7 = 7x_2.\end{aligned}\quad (3.15)$$

Next, he said: *It is evident that the general integral solution of (3.14) is derived from  $x_2 = k$ , where  $k$  is any positive integer, and consequently although (3.14) has an infinite number of integral solutions, all of them derive from  $x_2 = k$ , and consist merely of multiplies of values for the respective variables established by (3.15). All solutions other than for  $k = 1$ , are therefore trivial chemically as well as mathematically.*

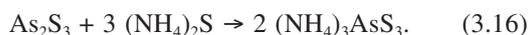
Unfortunately, the above statement is fallacious! The last sentence *All solutions other than for  $k = 1$ , are therefore trivial chemically as well as mathematically*, is incorrect. Previous Porges stated that  $x_2 = k$ , where  $k$  is any positive integer, and after that he took  $k = 1$ . It is wrong! Why? To this question a very simple answer will follow like this. The reaction (3.13) has a unique solution. If we substitute (3.15) into (3.13), and after that if we divide the relation (3.13) by an arbitrary real number  $x_2 \neq 0$ , immediately follows



Actually, Porges considered the general solution (3.15) of the system (3.14) separately of (3.13), what is wrong. The reaction (3.13) and the general solution (3.15) of the system (3.14) must be considered as one whole, because they are connected with each other.

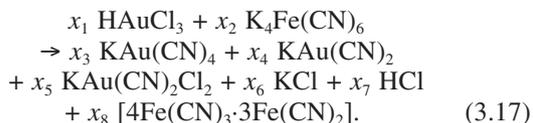
Obviously, we did not introduce any constant  $k$ , as it was done previously by Porges. Our approach is completely different than Porges' wrong way he used.

The same remark also holds for the second Porges' reaction



considered in<sup>41</sup>.

The third considered reaction in<sup>41</sup> is given by this expression

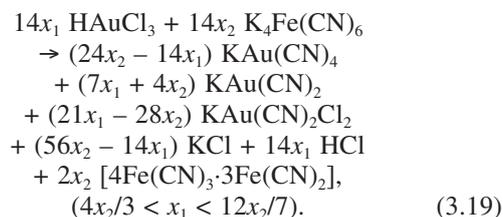


For its »solution« the author offered these expressions

$$\begin{aligned}x_1 &= 12k - 2, x_2 = 7k, x_3 = 2, x_4 = 8k - 1, \\x_5 &= 4k - 3, x_6 = 16k + 2, \\x_7 &= 12k - 2, x_8 = k,\end{aligned}\quad (3.18)$$

where  $k$  takes on all positive integral values. Yet (3.18) is merely a particular solution, but it is not the general solution of (3.17).

The general solution of the reaction (3.17) is given by this expression



The balanced reaction (3.19) is an expression of two parameters, but it is not one-parametric expression as it is given in<sup>41</sup>. In fact, it is another Porges' fallacy.

**Remark 3.7.** *Intentionally, we omitted from consideration other particular solutions of (3.19) because we had into account that our work has a limited size.*

Before ending his article<sup>41</sup>, Porges posed the following three questions:

1° *Is there, for equations of this third type which admits infinitely many distinct, not multiple solutions, a least action principle similar to that in mechanics?*

2° *Of the unlimited number of ways of balancing such an equation as (3.17), is that corresponding to the solution in least integer of the linear equations the one invariably indicated by the laboratory work, which is, after all, the real criterion?*

3° *Further, what would a minimum solution be – that for which the square root of the arithmetic mean of the squares of the variables is less than for any other solution?*

To date we did not meet in chemical literature any reply on these questions. It is a challenge for us to try to give appropriate answers on the above questions. Sure, the answers will be given in a rough form, because a comprehensive replay looks for a special article dedicated only on that particular subject.

The answer on the first question should be like this. *No! In chemistry there is not a least action principle similar to that in mechanics, because the balancing chemical equation has not any tangent point with mechanics, just it is connected with linear algebra. In fact, balancing chemical equations is not chemistry; it is just linear algebra<sup>7</sup>. On the other hand, the term a least action associate on the dynamism of 18<sup>th</sup> century as metaphysics was traced by Leibniz and Boscovich. Later Boyle gave an explicit formulation of chemistry in a coherent metaphysical scheme. A comprehensive study about metaphysics of chemical reaction is given in<sup>42</sup>.*

The second question is interesting for a discussion, and it can be answered negatively in this way. *Unlimited number of ways of balancing such a reaction as (3.17) is not corresponding to the solution in least integer of the linear equations the one invariably indicated by the laboratory work, which is, after all, the real criterion. This case, in fact, boils down to the continuum problem. It is an extremely hard problem, which is a stumbling block*

for mathematicians as well as chemists. In other words, this case can sink into the third question.

As the third question is posed, it contains a wrong formulation for minimum solution. It is one more Porges' fallacy. One can reply the last question like this. When the question is posed it was unbelievable for that time. It was impossible because the mathematical methods needed for its proof were unknown. For instance, Moore–Penrose pseudoinverse matrix<sup>8,9</sup> was discovered ten years later in 1955 and its first application in chemistry<sup>43</sup> appeared more than two decades later in 1978. Also, then was unknown the general problem of balancing chemical equations<sup>44</sup>. From today viewpoint, by using of Moore–Penrose pseudoinverse matrix the minimal solution is obtained in<sup>45,46</sup>.

Now, a new question arises: why not look for a topology of solutions of chemical equations, instead of finding minimal solutions? It is a much better question, than non-unique equation to be reduced to a minimal case. The question is new, and it is extremely hard. Sure, it will be a challenge for the next research.

Porges finished his article<sup>41</sup> on this way: In the very few equations of the third type encountered by the writer, the balancing in least integers was always that for which  $k$  was also least, and was identical with the laboratory balancing; but given a general solution not minimized by smallest admissible value of  $k$  – theoretically not impossible – then what?

It represents one last Porges' fallacy! We shall build the reply to this question on the concept of the *continuum*. In fact, the word *continuum* is recognizable as the name used by Cantor to refer to the real line. From the expression (3. 19), we can see that this kind of chemical equations reduces to the *Cantor's continuum problem*. This problem is simply condensed in the following question: How many points are there on the straight line in Euclidean space? In other words, the question is: How many different sets of integers do there exist?<sup>47</sup> This problem is neither simple nor easy; it needs a wide explanation. It shows that balancing chemical equations is a main object in **Foundation of Chemistry**, which lies in an intertwined mixture of topology, abstract algebra, linear algebra, axiomatic set theory, mathematical logic, computability theory and proof theory. To explain a little more fully this idea we must first discuss the concept of a *formal system*. Why? Simply, chemical equation must be treated only as a *formal system*, if we like to avoid appearance of paradoxes. In an opposite case we shall have paradoxes as these mentioned in this section.

A formal chemical system consists of a finite set of symbols and of a finite number of rules by which these symbols can be combined into formulas or statements. That kind of formal system is given in second section of this work. A number of such statements are nominated as axioms and by repeated applications of the rules of the system one obtains an ever growing body of provable statements.

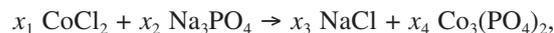
A proof of a given statement is a finite sequence of statements that starts with an axiom and ends with the preferred statement. The sequence is such that every transitional statement is either an axiom or is derivable by the rules of the system from statements that lead it. Thus, a statement that a sequence of formulas does or does not represent a proof of formula is »not« a statement in the formal system itself. It is a statement »about« the system and such statements are often referred to as »metamathematical«.

For the first time a formal generalized inverse matrix approach for balancing chemical equation is introduced in<sup>44</sup>. Balancing chemical equations as a matrix well-defined formal system is given in the works<sup>45,46,48–50</sup>.

**III.** Another paradox in the theory of balancing chemical equations is the following Standen's statement<sup>38</sup>: It would seem that examples could not be found where the number of mathematical equations actually exceeds the number of variables; for if the mathematical equations were inconsistent, the whole thing would be an impossibility, while if they were consistent it would indicate that the chemical equation had been appropriately broken down into its terms.

To prove the above Standen's absurdity, we shall use the following counterexamples.

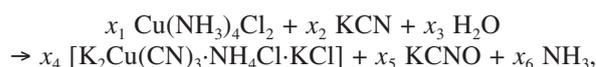
**Example 3.8.** The chemical reaction



contains five elements involved in four molecules, *i. e.*, in this case the chemical reaction reduces to a system of five linear equations in four unknown variables and the chemical reaction has a unique solution. The balanced reaction has this form

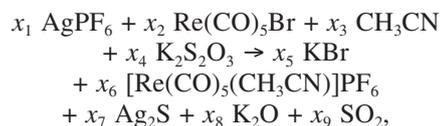


**Example 3.9.** In this particular reaction



are involved seven elements in six molecules, *i. e.*, we have seven linear equations in six unknown variables. The chemical reaction has a unique solution  $x_1 = 2$ ,  $x_2 = 7$ ,  $x_3 = 1$ ,  $x_4 = 2$ ,  $x_5 = 1$ ,  $x_6 = 6$ .

**Example 3.10.** For instance, the chemical reaction



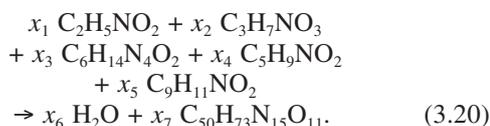
has eleven elements involved in nine molecules. The above chemical reaction reduces to a system of eleven linear equations in nine unknown variables, whose unique solution is  $x_1 = 4$ ,  $x_2 = 4$ ,  $x_3 = 4$ ,  $x_4 = 3$ ,  $x_5 = 4$ ,  $x_6 = 4$ ,  $x_7 = 2$ ,  $x_8 = 1$ ,  $x_9 = 4$ .

By the last three counterexamples we showed that the above Standen's<sup>38</sup> statement is an absurd.

**IV.** Next, we shall consider the Blakley's<sup>51</sup> paradox. Among other chemical reactions, he considered hydroly-

sis of two organic substances: *bradykinin* and *gramicidin-S*.

**Example 3.11.** The following reaction



was studied in<sup>51</sup>. Blakley considered balancing of the above chemical reaction by a matrix approach using a module basis.

He »proved« that »hydrolysis (3.20) of *bradykinin* is unique«. It represents only an empirical discovered relationship, which is wrong.

We shall prove the absurdity of his statement by using the well-known algebraic method for balancing chemical equations.

By the way, we shall show that this method is powerful and its usage is not limited as some traditional oriented chemists think.

Let us consider the scheme of the chemical reaction (3.20).

	$\text{C}_2\text{H}_5\text{NO}_2$	$\text{C}_3\text{H}_7\text{NO}_3$	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$	$\text{C}_5\text{H}_9\text{NO}_2$	$\text{C}_9\text{H}_{11}\text{NO}_2$	$\text{H}_2\text{O}$	$\text{C}_{50}\text{H}_{73}\text{N}_{15}\text{O}_{11}$
C	2	3	6	5	9	0	-50
H	5	7	14	9	11	-2	-73
N	1	1	4	1	1	0	-15
O	2	3	2	2	2	-1	-11

From the above scheme immediately follows the stoichiometric matrix

$$A = \begin{bmatrix} 2 & 3 & 6 & 5 & 9 & 0 & -50 \\ 5 & 7 & 14 & 9 & 11 & -2 & -73 \\ 1 & 1 & 4 & 1 & 1 & 0 & -15 \\ 2 & 3 & 2 & 2 & 2 & -1 & -11 \end{bmatrix}$$

with  $r = \text{rank}A = 4$ .

Since  $\text{nullity}A = n - r = 7 - 4 = 3 > 1$ , where  $n$  is the total number of reaction molecules, then the chemical reaction is possible and it has an infinite number of solutions. Let us prove it.

One can reduce the chemical reaction (3.20) to the following system of linear equations

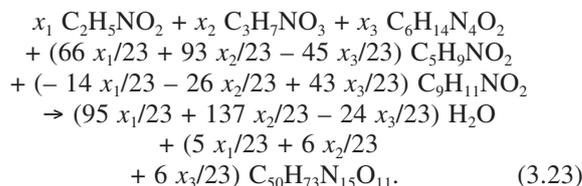
$$\begin{aligned} 2x_1 + 3x_2 + 6x_3 + 5x_4 + 9x_5 &= 50x_7, \\ 5x_1 + 7x_2 + 14x_3 + 9x_4 + 11x_5 &= 2x_6 + 73x_7, \\ x_1 + x_2 + 4x_3 + x_4 + x_5 &= 15x_7, \\ 2x_1 + 3x_2 + 2x_3 + 2x_4 + 2x_5 &= x_6 + 11x_7. \end{aligned} \quad (3.21)$$

The general solution of the system (3.21) is given by the following expressions

$$\begin{aligned} x_4 &= 66x_1/23 + 93x_2/23 - 45x_3/23, \\ x_5 &= -14x_1/23 - 26x_2/23 + 43x_3/23, \\ x_6 &= 95x_1/23 + 137x_2/23 - 24x_3/23, \\ x_7 &= 5x_1/23 + 6x_2/23 + 6x_3/23, \end{aligned} \quad (3.22)$$

where  $x_i > 0$  ( $1 \leq i \leq 3$ ) are arbitrary real numbers.

After substitution of (3.22) in (3.20), one obtains a balanced chemical reaction



From (3.23) follows this system of inequalities

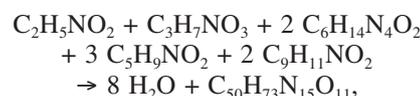
$$\begin{aligned} 22x_1 + 31x_2 - 15x_3 &> 0, \\ -14x_1 - 26x_2 + 43x_3 &> 0, \\ 95x_1 + 137x_2 - 24x_3 &> 0, \\ 5x_1 + 6x_2 + 6x_3 &> 0. \end{aligned} \quad (3.24)$$

From the first and the second inequality of (3.24) immediately follows this expression

$$\begin{aligned} 14x_1/43 + 26x_2/43 &< x_3 \\ &< 22x_1/15 + 31x_2/15. \end{aligned} \quad (3.25)$$

The expression (3.25), the third and the fourth inequality of (3.24) are necessary and sufficient conditions for (3.23) to hold.

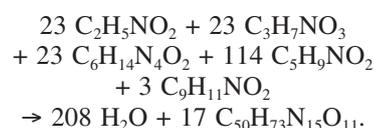
For instance, if we substitute  $x_1 = x_2 = 1$  and  $x_3 = 2$  in (3.23), then as a particular case appears this reaction



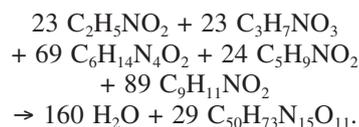
for which Blakley<sup>51</sup> stated that it is unique, but it is not true.

Now, we shall give two more particular cases for which (3.23) holds.

Let  $x_1 = x_2 = x_3 = 1$ , then from (3.23) one obtains the reaction

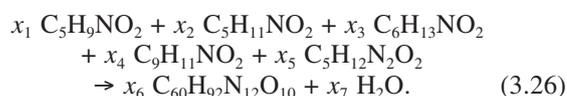


Let  $x_1 = x_2 = 1$  and  $x_3 = 3$ , then (3.23) becomes



The other particular cases of (3.23) are not considered, because we took into account the Remark 3.7.

**Example 3.12.** In<sup>51</sup> the hydrolysis of *gramicidin-S* was studied, given by the following reaction



For the chemical reaction (3.26) if we write its stoichiometric scheme, then one obtains

	$C_5H_9NO_2$	$C_5H_{11}NO_2$	$C_6H_{13}NO_2$	$C_9H_{11}NO_2$	$C_5H_{12}N_2O_2$	$C_{60}H_{92}N_{12}O_{10}$	$H_2O$
C	5	5	6	9	5	-60	0
H	9	11	13	11	12	-92	-2
N	1	1	1	1	2	-12	0
O	2	2	2	2	2	-10	-1

from where follows the stoichiometric matrix

$$A = \begin{bmatrix} 5 & 5 & 6 & 9 & 5 & -60 & 0 \\ 9 & 11 & 13 & 11 & 12 & -92 & -2 \\ 1 & 1 & 1 & 1 & 2 & -12 & 0 \\ 2 & 2 & 2 & 2 & 2 & -10 & -1 \end{bmatrix}$$

with  $r = \text{rank}A = 4$ .

Since  $\text{nullity}A = n - r = 7 - 4 = 3 > 1$ , then chemical reaction is possible and it has an infinity number of solutions. Let us prove it.

The system of linear equations obtained from (3.26) is

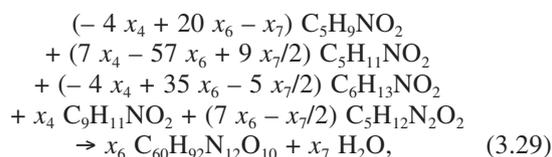
$$\begin{aligned} 5x_1 + 5x_2 + 6x_3 + 9x_4 + 5x_5 - 60x_6 &= 0, \\ 9x_1 + 11x_2 + 13x_3 + 11x_4 + 12x_5 - 92x_6 - 2x_7 &= 0, \\ x_1 + x_2 + x_3 + x_4 + 2x_5 - 12x_6 &= 0, \\ 2x_1 + 2x_2 + 2x_3 + 2x_4 + 2x_5 - 10x_6 - 1x_7 &= 0. \end{aligned} \quad (3.27)$$

The general solution of (3.27) is given by the expressions

$$\begin{aligned} x_1 &= -4x_4 + 20x_6 - x_7, \\ x_2 &= 7x_4 - 57x_6 + 9x_7/2, \\ x_3 &= -4x_4 + 35x_6 - 5x_7/2, \\ x_5 &= 7x_6 - x_7/2, \end{aligned} \quad (3.28)$$

where  $x_4$ ,  $x_6$  and  $x_7$  are arbitrary real numbers.

After substitution of (3.28) in (3.26), the balanced chemical reaction has this form



From (3.29) follows this system of inequalities

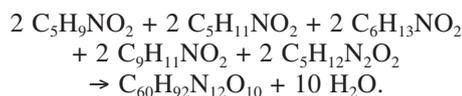
$$\begin{aligned} -4x_4 + 20x_6 - x_7 &> 0, \\ 7x_4 - 57x_6 + 9x_7/2 &> 0, \\ -4x_4 + 35x_6 - 5x_7/2 &> 0, \\ 7x_6 - x_7/2 &> 0. \end{aligned} \quad (3.30)$$

From the second and the third inequality of (3.30) immediately follows this expression

$$\begin{aligned} -14x_4/9 + 114x_6/9 &< x_7 \\ &< -8x_4/5 + 14x_6. \end{aligned} \quad (3.31)$$

The expression (3.31), the first and the fourth inequality of (3.30) are necessary and sufficient conditions for (3.29) to hold.

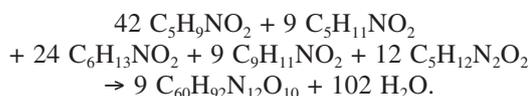
For instance, if we substitute  $x_4 = 2$ ,  $x_6 = 1$  and  $x_7 = 10$  in (3.29), then as a particular case appears this reaction



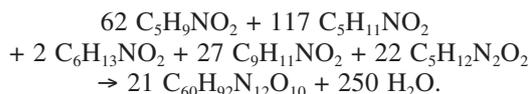
for which Blakley<sup>51</sup> stated that it is unique, but it is not true.

Now, we shall give more two particular cases for which holds (3.29).

Let  $x_4 = x_6 = 9$  and  $x_7 = 102$ , then from (3.29) one obtains the reaction



Let  $x_4 = 27$ ,  $x_6 = 21$  and  $x_7 = 250$ , then (3.29) becomes



The other particular cases of (3.29) are not considered because we took into account the Remark 3.7.

V. Das in his article<sup>52</sup> applied the partial equation method for balancing chemical equations. There he wrote: *if the number of reactants and products is equal to or less (or at most one more) than the total number of elements involved in the chemical equation, then there will be only one way of balancing a chemical equation.*

For the first two cases this statement is a paradox! The next two counterexamples given below contradict to the above statement.

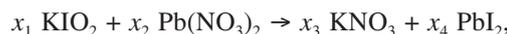
**Example 3.13.** The following chemical reaction



has involved four elements in four molecules, but it has not a unique solution as stated above. It is an unfeasible reaction, because  $x_1 = x_2 = x_3 = x_4 = 0$ .

Now, we shall give another counterexample.

**Example 3.14.** In the reaction

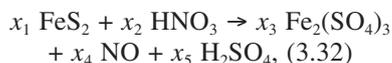


five elements are involved in four molecules. This reaction has only a trivial solution  $x_1 = x_2 = x_3 = x_4 = 0$ . It shows that this reaction is unfeasible.

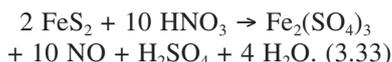
VI. Next, we shall elaborate another very interesting paradox. García<sup>53</sup> gave a »half-reaction method« for balancing chemical equations. He described his »method« on this way. *The chemical reaction is divided into two half-reactions and each one is balanced independently. These two balanced half-reactions are added together to*

get the correct stoichiometry of the reaction. One half-reaction is formed with compounds that contain the same elements other than oxygen and hydrogen. The remaining compounds, and others if it is necessary, constitute the other half-reaction.

**Example 3.15.** This chemical reaction



he »balanced« like this



Unfortunately reaction (3.33) is quantitatively and qualitatively different from the reaction (3.32). Actually, the reaction (3.33) is augmented reaction (3.32) by four water molecules. Reactions (3.32) and (3.33) belong to different types of reactions, and according to it, they are incompatible. The reaction (3.32) belongs to the type of unfeasible reactions, because its vectors of molecules do not generate a vector space  $V$  over  $\mathfrak{R}$ .

For our next analysis we shall use the newest method<sup>7</sup> for balancing chemical equations founded by virtue of theory of complex finite dimensional vector spaces. We chose it, because in this particular Garcia's case, it was the most suitable method for comparative analysis of chemical reactions which belong to different classes. Application of this method confirmed its scientific supremacy.

From (3.32) one obtains the scheme given below

	$v_1 = \text{FeS}_2$	$v_2 = \text{HNO}_3$	$v_3 = \text{Fe}_2(\text{SO}_4)_3$	$v_4 = \text{NO}$	$v_5 = \text{H}_2\text{SO}_4$
Fe	1	0	2	0	0
S	2	0	3	0	1
H	0	1	0	0	2
N	0	1	0	1	0
O	0	3	12	1	4

The vector equation of reaction (3.32) is

$$x_1 v_1 + x_2 v_2 = x_3 v_3 + x_4 v_4 + x_5 v_5,$$

i. e.,

$$x_1 (1, 2, 0, 0, 0)^T + x_2 (0, 0, 1, 1, 3)^T = x_3 (2, 3, 0, 0, 12)^T + x_4 (0, 0, 0, 1, 1)^T + x_5 (0, 1, 2, 0, 4)^T,$$

or

$$(x_1, 2x_1, x_2, x_2, 3x_2)^T = (2x_3, 3x_3 + x_5, 2x_5, x_4, 12x_3 + x_4 + 4x_5)^T.$$

The system of linear equations

$$x_1 = 2x_3, \quad 2x_1 = 3x_3 + x_5, \quad x_2 = 2x_5, \quad x_2 = x_4, \quad 3x_2 = 12x_3 + x_4 + 4x_5,$$

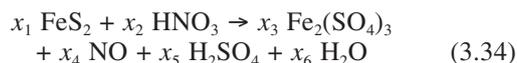
is inconsistent, because one obtains the contradiction  $x_5 = x_1/2$  and  $x_5 = -x_1$ . It means that the vectors  $v_1, v_2, v_3, v_4$  and  $v_5$  of molecules of the chemical reaction (3.32) are linearly independent and they do not generate a vector space  $V$  over  $\mathfrak{R}$ . By this we showed that the chemical reaction (3.32) is unfeasible.

On the other hand, the rank of the reaction matrix  $A$  of the chemical reaction (3.32) is

$$r = \text{rank} A = \text{rank} \begin{bmatrix} 1 & 0 & 2 & 0 & 0 \\ 2 & 0 & 3 & 0 & 1 \\ 0 & 1 & 0 & 0 & 2 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 3 & 12 & 1 & 4 \end{bmatrix} = 5$$

According to the algebraic criterion (2.6) for balancing chemical reactions, the reaction (3.32), has nullity  $A = n - r = 5 - 5 = 0$ , that means that the reaction (3.32) is unfeasible. Both proofs, vector and algebraic, confirmed the same, that the reaction (3.32) is unfeasible. It contradicts the Garcia's »procedure« named as »half-reaction method« for balancing chemical reactions.

Now, we shall consider the reaction (3.33) in its unbalanced form



Now, we need the stoichiometric scheme for the above chemical reaction. From this particular reaction (3.34), we shall derive very easy required stoichiometric scheme

	$v_1 = \text{FeS}_2$	$v_2 = \text{HNO}_3$	$v_3 = \text{Fe}_2(\text{SO}_4)_3$	$v_4 = \text{NO}$	$v_5 = \text{H}_2\text{SO}_4$	$v_6 = \text{H}_2\text{O}$
Fe	1	0	2	0	0	0
S	2	0	3	0	1	0
H	0	1	0	0	2	2
N	0	1	0	1	0	0
O	0	3	12	1	4	1

From the above scheme one obtains this vector equation

$$x_1 v_1 + x_2 v_2 = x_3 v_3 + x_4 v_4 + x_5 v_5 + x_6 v_6,$$

i. e.,

$$x_1 (1, 2, 0, 0, 0)^T + x_2 (0, 0, 1, 1, 3)^T = x_3 (2, 3, 0, 0, 12)^T + x_4 (0, 0, 0, 1, 1)^T + x_5 (0, 1, 2, 0, 4)^T + x_6 (0, 0, 2, 0, 1)^T,$$

or

$$(x_1, 2x_1, x_2, x_2, 3x_2)^T = (2x_3, 3x_3 + x_5, 2x_5 + 2x_6, x_4, 12x_3 + x_4 + 4x_5 + x_6)^T.$$

The solution of the system of linear equations

$$\begin{aligned}x_1 &= 2x_3, 2x_1 = 3x_3 + x_5, x_2 = 2x_5 + 2x_6, \\x_2 &= x_4, 3x_2 = 12x_3 + x_4 + 4x_5 + x_6,\end{aligned}$$

is

$$\begin{aligned}x_2 &= 5x_1, x_3 = x_1/2, x_4 = 5x_1, \\x_5 &= x_1/2 \text{ and } x_6 = 2x_1.\end{aligned}\quad (3.35)$$

If we substitute (3.35) in (3.34), and after that, if we divide the reaction by  $x_1/2$  one obtains (3.33). The vectors  $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$  and  $\nu_6$  of reaction molecules are linearly dependent and they generate a vector space  $V$  over  $\mathfrak{R}$ . By this we confirmed that the reaction (3.33) has a unique solution.

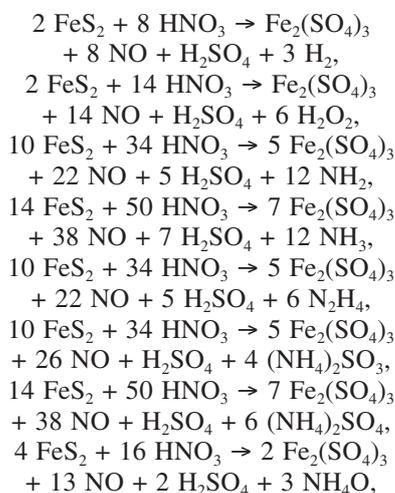
Similarly as in the previous equation analysis, now we can go to the next step. Now we can calculate the rank of the reaction matrix  $A$  of the reaction (3.33).

Therefore, we can express its rank in this way

$$r = \text{rank}A = \text{rank} \begin{bmatrix} 1 & 0 & 2 & 0 & 0 & 0 \\ 2 & 0 & 3 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 2 & 2 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 3 & 12 & 1 & 4 & 1 \end{bmatrix} = 5$$

According to the algebraic criterion (2.6) for balancing chemical equations, the reaction matrix  $A$  has  $\text{nullity}A = n - r = 6 - 5 = 1$ . By this, again we showed that chemical reaction (3.33) has a unique solution. The analysis of the reaction (3.33), established that it belongs to the type of solvable equations, which have a unique solution.

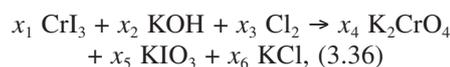
This comparative analysis confirmed that García's half-reaction simple *»method«*<sup>53</sup> is completely wrong. Generally speaking, his so-called *»method«* cannot recognize the type of reaction, and much less to decide if the chemical equation is solvable or not. To support it, we shall give a dozen of counterexamples, where water molecules in García's procedure of reaction extension (3.33), may be substituted by other molecules of the elements involved in the reaction (3.32), as it is exposed by the following reactions



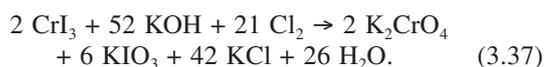
Neither one of the above reactions nor chemical reaction (3.33) is equivalent to the chemical reaction (3.32). Therefore, reactions (3.32) and (3.33) are incompatible.

In a similar way, García considered the following two reactions<sup>53</sup>.

**Example 3.16.** The following chemical reaction



he *»balanced«* like this



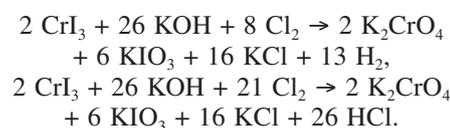
On top of all he said: *This method is appropriate to balance any kind of reaction, even those that include complex ions or reactions of compounds with oxidation numbers difficult to determine.*

By the same analysis which we used in the previous counterexample, very easy we shall show the absurdity of his statement.

Reaction (3.36) belongs to the type of unfeasible reaction. Its stoichiometric matrix  $A$  has rank  $r = \text{rank}A = 6$  and its  $\text{nullity}A = n - r = 6 - 6 = 0$  verifies that it is an unfeasible reaction. Also, this reaction generates an inconsistent system of linear equations which has only a trivial solution  $x_i = 0$ , ( $1 \leq i \leq 6$ ). Thus, this algebraic criterion verifies that the reaction (3.36) is unfeasible too.

Reaction (3.37) generates a consistent system of linear equations which has a unique solution given in (3.37). Also, the  $\text{nullity}A = n - r = 7 - 6 = 1$ , shows that this equation has a unique solution. Therefore, reactions (3.36) and (3.37) are incompatible, because they are two completely different types of reactions – the first one is an unfeasible reaction, while the second one is a unique reaction.

Now, we shall mention just two chemical reactions, where water molecules in García's *»procedure«* of reaction extension (3.37), are substituted by other molecules of the elements involved in the reaction (3.36):



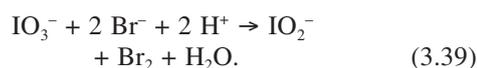
Neither one of the above reactions nor chemical reaction (3.37) is equivalent to the chemical reaction (3.36). Therefore, reactions (3.36) and (3.37) are incompatible.

In the same paper, García considered two ionic reactions too. Unfortunately, also in these particular cases the same absurdity appears again.

**Example 3.17.** For example, he *»balanced«* an unfeasible reaction



where  $x_i = 0$  ( $1 \leq i \leq 4$ ) as a unique reaction



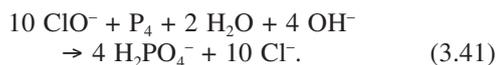
Reactions (3.38) and (3.39) are two completely different reactions and they are incomparable!

A second ionic example that García considered is given in the next example.

**Example 3.18.** The reaction



is »balanced« like this



Where is the hydrogen atom in the left side of (3.40)? Reaction (3.40) is an *absurd*, because it does not contain hydrogen atom in its left side. **With this kind of reactions current chemistry does not work!**

Reaction (3.41) does not depend on (3.40) and it represents a solvable equation. In other words, reactions (3.40) and (3.41) are completely different types of reactions and they are incompatible.

**VII.** In<sup>54</sup> the so-called »formal balance numbers« (FBN) are introduced like this: *Formal balance numbers are an aid that may grossly facilitate the problem of balancing complex redox equations. They may be chosen as being equal to the traditional values of oxidation numbers, but not necessarily. An inspection of the redox equation may suggest the optimal values that are to be assigned to formal balance numbers. In most cases, these optimal values ensure that only two elements will 'change their state' (i. e. the values of the formal balance numbers), allowing the use of the oxidation number technique for balancing equations, in its simplest form. Just as for oxidation numbers, the algebraic sum of the formal balance numbers in a molecule/neutral unit is 0, while in an ion it is equal to its charge (the sum rule).*

It was quickly detected that the »procedure« given in<sup>54</sup> boils down to using of well-known *unconventional oxidation numbers*, which previously were advocated by Tóth<sup>55</sup> and Ludwig<sup>56</sup>.

Consider this sentence from previous definition: *They may be chosen as being equal to the traditional values of oxidation numbers, but not necessarily.* It is a *paradox!* If the »formal balance numbers« can be the same as *oxidation numbers* or not, then the whole definition is illogical. This definition represents only a contradictory premise, which does not have any correlation with balancing chemical equations. It is just one thing.

Another thing, the above definition does not speak anything about balancing chemical reactions in a chemical sense of the word, or their solution in a mathematical sense.

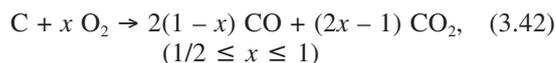
Recent research<sup>7</sup> confirmed that **a chemical equation can be balanced if and only if it generates a vector space.** That is a necessary and sufficient condition for balancing a chemical equation!

The so-called **called** »formal balance numbers«, which actually are the same as the well-known *oxidation numbers*, **do not represent any criterion for balancing chemical equations.**

Also the author of<sup>54</sup> asserted that his »procedure« is *probably the fastest of all possible methods!* Obviously the author omitted to *prove* it. **Perhaps, his statement is valid (if he can prove it?) in some metachemistry, but from a viewpoint of current mathematics and chemistry it is not true.** Why? The reason is very simple. In mathematics, as well as in chemistry there is neither a definition for speed of equation solution nor its unit, and according to it, it is impossible to compare which method is faster. It is just one thing; another thing is that the definition of so-called »formal balance numbers« (FBN)<sup>54</sup> is paradoxical and it produces only inconsistent procedure for balancing chemical equations. According to it, the author's assertion of<sup>54</sup> is an absurd.

The »procedure«<sup>54</sup> founded by virtue of so-called »formal balance numbers« (FBN), with several counterexamples was refuted in<sup>7</sup>.

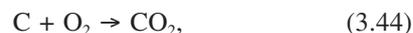
**VIII.** Ten Hoor in<sup>57</sup> obtained this result:



*if the coefficient of a product is allowed to be equal to zero. Taking  $x$  equal to its smallest or largest extreme value, equation (3.42) reduces to*

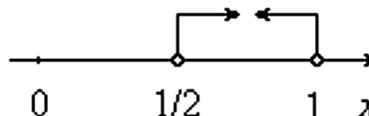


*or*



*respectively.*

The above statement is wrong. The reaction (3.42) holds if only if  $1/2 < x < 1$ , like it is shown on Fig. 2, but not as it is given in<sup>57</sup>.

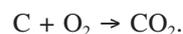


**Figure 2:** The interval  $1/2 < x < 1$

In (3.42)  $x$  does not have any extreme value, because it is presented by the following linear functions:  $x$ ,  $2-2x$  and  $2x-1$ . None of these functions have extrema, since their second derivatives are equal to zero. Then on what basis ten Hoor<sup>57</sup> states that for smallest or largest extreme value of  $x$  the reaction (3.42) reduces to (3.43) and (3.44) respectively?

The chemical reaction (3.42) has two subgenerators  $2-2x$  and  $2x-1$  which generate the following particular cases:

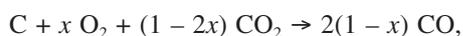
1° For  $x = 1$ , then (3.42) reduces to



2° For  $x = 1/2$ , then (3.42) becomes



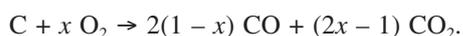
3° For  $x < 1/2$ , then (3.42) transforms into



4° For  $x > 1$ , then from (3.42) one obtains

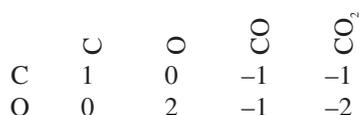


5° For  $1/2 < x < 1$ , holds this reaction



Next, for the reaction (3.42) we shall determine its minimal coefficients by using of Moore–Penrose generalized inverse matrix<sup>46</sup>.

From the chemical reaction (3.42) follows this scheme



According to the above scheme, the reaction matrix  $A$  of (3.42) has this form

$$A = \begin{bmatrix} 1 & 0 & -1 & -1 \\ 0 & 2 & -1 & -2 \end{bmatrix}$$

The Moore–Penrose generalized inverse matrix  $A^+$  is

$$A^+ = A^T(A A^T)^{-1} = \begin{bmatrix} 1/2 & -1/6 \\ -1/3 & 1/3 \\ -1/3 & 0/0 \\ -1/6 & -1/6 \end{bmatrix}$$

The reaction (3.42) reduces to this matrix form

$$A\mathbf{x} = \mathbf{0}, \quad (3.45)$$

where  $\mathbf{x} = (x_1, x_2, x_3, x_4)^T$  is the vector of the coefficients of (3.42),  $\mathbf{0} = (0, 0)^T$  is the zero vector and T denoting transpose.

The general solution of the matrix equation (3.45) is

$$\mathbf{x} = (\mathbf{I} - A^+A)\mathbf{a}, \quad (3.46)$$

where  $\mathbf{a}$  is an arbitrary vector and  $\mathbf{I}$  is a unite matrix. For  $\mathbf{a} = (1, 1, 1, 1)^T$ , one obtains

$$\mathbf{x}_{min} = (4/3, 1, 2/3, 2/3)^T.$$

Then the reaction (3.42) with its minimal coefficients attains this form



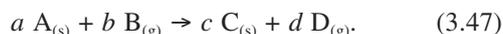
but not as ten Hoor asserted in<sup>57</sup>. By this proof we have shown that his statement is paradoxical.

Also, the assumptions 1 and 2 which ten Hoor used in<sup>57</sup> are completely wrong, because carbon burns according to the Boudouard's reaction<sup>58</sup>. Wrong suppositions can not lead to correct results.

**IX.** Authors of the article<sup>59</sup> studied several chemical reactions, but unfortunately there are given lots of erroneous results.

Let us mention them. In their article<sup>59</sup> they provided the following wrong definition: *a chemical equation is a written representation of a chemical reaction, showing the reactants and products, they physical states, and the direction in which the reaction proceeds.*

According to the above definition a chemical equation will show like this



For instace, if  $r = s = 2$  in (2.1), then as a particular case appears the reaction (3.47). Actually, *it is not a definition for a chemical equation*, just opposit it is *a definition for a chemical reaction*. Obviously the authors can not distinguish what is a *chemical reaction* and what is its *chemical equation*. These two things are different entities given by the Definitions 2.2 and 2.1 (in a descriptive form), *i.e.*, 2.11 (in an analitical form), respectively. It is just one reason what the above definition is wrong.

In order to be balanced certain chemical reaction is not necessary to be known its reactants and products as it is described in the above definition! It holds if only if reaction is given in a conventional form, but in an opposite case it does not hold. For instace, the chemical reaction (3.47) given in a convntional form can be presented in an algebrical free form too

$$a A_{(s)} + b B_{(g)} + c C_{(s)} + d D_{(g)} = 0. \quad (3.48)$$

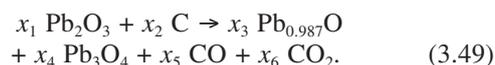
After determination of its coefficients, one obtains that some of them have a negative sign and others have a positive sign. Positive coefficients stay in front of reactants and negative coefficients stay in front of products of reaction, that means that chemical reaction is self-adaptive. For example, in<sup>48</sup> are balanced chemical reactions given in an algebrical free form.

Next, we shall give an another reason why the above definition is wrong.

Chemical equation does not have arrow mark as a reaction, just sign for equality. It is a main difference between chemical reaction and chemical equation.

More accurately speaking, **any chemical reaction has a chemical equation, but the opposite does not hold.** Why?

Next, we shall give an explanation about it by a new example. Let us balance the following chemical reaction



From the above reaction follows this system of linear equations

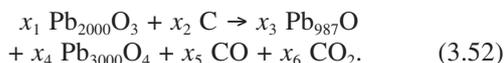
$$\begin{aligned} 2x_1 &= 0.987x_3 + 3x_4, \\ 3x_1 &= x_3 + 4x_4 + x_5 + 2x_6, \\ x_2 &= x_5 + x_6. \end{aligned} \quad (3.50)$$

In order to avoid fractional coefficients of the system (3.50), we shall multiply its first equation by 1000, such that one obtains this system of linear equations

$$\begin{aligned} 2000 x_1 &= 987 x_3 + 3000 x_4, \\ 3 x_1 &= x_3 + 4 x_4 + x_5 + 2 x_6, \\ x_2 &= x_5 + x_6. \end{aligned} \quad (3.51)$$

The systems (3.50) and (3.51) are equivalent and they have same solution.

Now, according to the system (3.51) the chemical reaction (3.49) will transform into this particular form



Do the expression (3.52) is a correct chemical reaction? No! It represents only an ordinary chemical absurd, because the molecules  $\text{Pb}_{2000}\text{O}_3$ ,  $\text{Pb}_{987}\text{O}$  and  $\text{Pb}_{3000}\text{O}_4$  do not exist in chemistry. This is the cause why from chemical equation does not follow chemical reaction.

Chemical reactions (3.49) and (3.52) in a mathematical sense both are equivalent reactions, since they reduce to the same system of linear equations, but in a chemical sense they are not equivalent reactions. That means, that

*math. equivalency*  $\neq$  *chem. equivalency*.

In other words, from a mathematical point of view, the systems (3.50) and (3.51) both are equivalent, but from a chemical view point they are not, since they generate different chemical reactions.

The above explanation, we can articulate roughly on this way: performing of reaction is a chemical subject, and its balancing is a mathematical topic. This is the reason why balancing of chemical reactions is pure mathematical matter, but not a chemical issue.

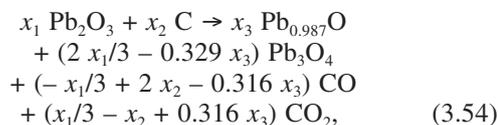
Next, we shall continue with the balancing of the reaction (3.49), because its general solution is necessary for a comparative analysis of other particular chemical reactions.

The general solution of the system (3.50) is

$$\begin{aligned} x_4 &= 2 x_1/3 - 0.329 x_3, \\ x_5 &= -x_1/3 + 2 x_2 - 0.316 x_3, \\ x_6 &= x_1/3 - x_2 + 0.316 x_3, \end{aligned} \quad (3.53)$$

where  $x_i$ , ( $1 \leq i \leq 3$ ) are arbitrary real numbers.

Balanced reaction has this form



where  $x_i$ , ( $1 \leq i \leq 3$ ) are arbitrary real numbers.

Since  $x_4$ ,  $x_5$  and  $x_6$  are  $> 0$ , then from (3.54) one obtains this system of inequalities

$$\begin{aligned} 2 x_1/3 - 0.329 x_3 &> 0, \\ -x_1/3 + 2 x_2 - 0.316 x_3 &> 0, \\ x_1/3 - x_2 + 0.316 x_3 &> 0. \end{aligned} \quad (3.55)$$

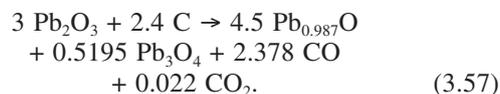
From (3.55), we obtain this relation

$$3 x_2 - 0.948 x_3 < x_1 < 6 x_2 - 0.948 x_3. \quad (3.56)$$

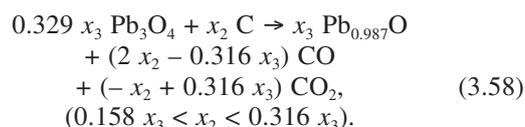
The inequality (3.56) is necessary and sufficient condition to hold the general reaction (3.54).

Now, we can analyze the general reaction (3.54) for all possible values of  $x_1$ ,  $x_2$  and  $x_3$ . As particular reactions of (3.54) we shall derive the following cases.

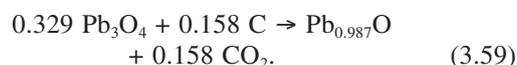
1° For  $x_1 = 3$ ,  $x_2 = 2.4$  and  $x_3 = 4.5$ , from (3.53) follows  $x_4 = 0.5195$ ,  $x_5 = 2.378$  and  $x_6 = 0.022$ , *i.e.*, one obtains this particular reaction



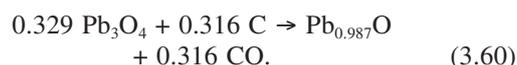
2° For  $x_1 = 0$ , the reaction (3.54) transforms into this particular reaction



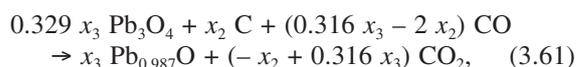
3° For  $x_2 = 0.158 x_3$ , from (3.58) one obtains



4° For  $x_2 = 0.316 x_3$ , the reaction (3.58) becomes

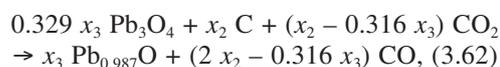


5° For  $x_2 < 0.158 x_3$ , from (3.58) follows



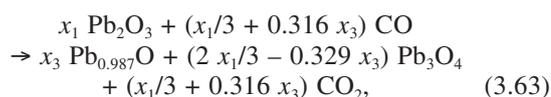
where  $x_2$  and  $x_3$  are arbitrary real numbers.

6° For  $x_2 > 0.316 x_3$ , the reaction (3.58) becomes



where  $x_2$  and  $x_3$  are arbitrary real numbers.

7° For  $x_2 = 0$ , from (3.54) one obtains this particular reaction



where  $x_1$  and  $x_3$  are arbitrary real numbers.

From (3.63) follows these inequalities

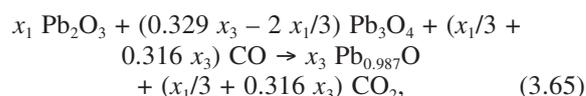
$$x_1/3 + 0.316 x_3 > 0 \text{ and } 2 x_1/3 - 0.329 x_3 > 0.$$

From this system follows this inequality

$$-x_1/0.048 < x_3 < 2 x_1/0.987. \quad (3.64)$$

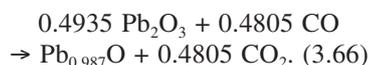
The reaction (3.63) holds if only if the inequality (3.64) is satisfied.

8° For  $x_1 < 0.4935 x_3$ , from (3.63) follows

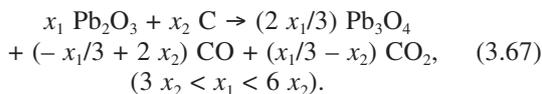


where  $x_1$  and  $x_3$  are arbitrary real numbers.

9° For  $x_1 = 0.4935 x_3$ , from (3.63) follows



10° For  $x_3 = 0$ , from (3.54) one obtains this particular reaction



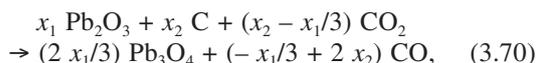
11° For  $x_1 = 3 x_2$ , from (3.67) follows



12° For  $x_1 = 6 x_2$ , from (3.67) one obtains

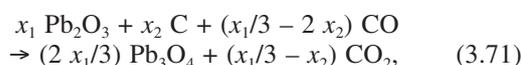


13° For  $x_1 < 3 x_2$ , from (3.67) follows



where  $x_1$  and  $x_2$  are arbitrary real numbers.

14° For  $x_1 > 6 x_2$ , the reaction (3.67) transforms into

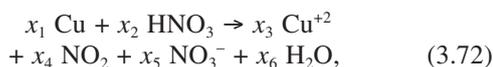


where  $x_1$  and  $x_2$  are arbitrary real numbers.

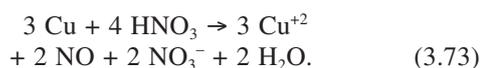
The authors of the article<sup>59</sup> gave this statement: *Balancing the chemical equation (with three molecules) means finding the smallest whole numbers  $x_1$ ,  $x_2$  and  $x_3$  (as its coefficients).*

The above statement does not hold for every reaction. It has just particular meaning and holds if only if a chemical reaction has atoms with integers, in an opposite case, when the reaction contains atoms with fractional oxidation numbers, it does not hold. For example, see the previous reactions (3.57), (3.58) and so on.

Also, in the article<sup>59</sup> is »balanced« this reaction

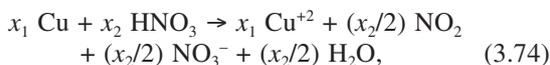


like this



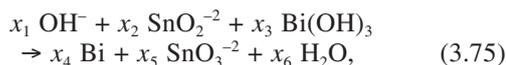
The last reaction (3.73) is wrong.

The correct form of balanced reaction (3.72) is

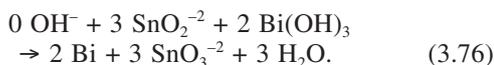


where  $x_1, x_2 > 0$  are arbitrary real numbers.

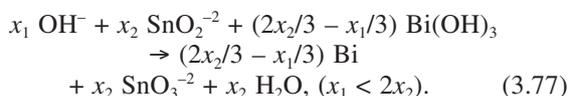
Next reaction was »balanced« in<sup>59</sup> too



in this form

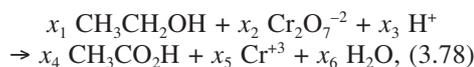


The general form of the reaction (3.75) is

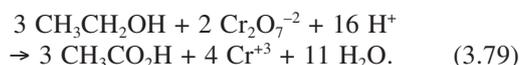


For  $x_1 = 0$  and  $x_2 = 3$ , from (3.77) immediately follows (3.76), like a particular reaction.

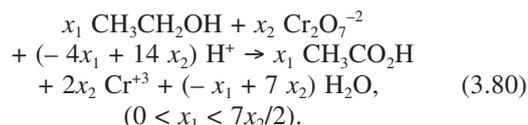
Another reaction is »balanced« in<sup>59</sup>



in this form



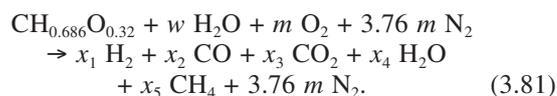
The general form of the reaction (3.78) is



For  $x_1 = 3$  and  $x_2 = 2$ , from (3.80) immediately follows (3.79), like a particular reaction.

In<sup>59</sup> the authors only determined the particular reactions (3.76) and (3.79), but considered reactions (3.75) and (3.78) have general forms with two arbitrary parameters, given by (3.77) and (3.80), respectively.

X. As a last paradox we discovered in the theory of balancing chemical equations is the case considered below. The authors of the article<sup>60</sup> studied this chemical reaction

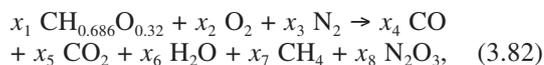


Immediately from (3.81) we have seen its absurdity. In this reaction  $\text{H}_2\text{O}$  appears as a reactant and as a product at the same time. Is it logical? No! It is just one thing.

Another illogical thing is not reacted  $\text{N}_2$ . Nitrogen appears in (3.81) as reactant  $3.76m \text{N}_2$  and  $3.76m \text{N}_2$  as a product at the same time.

Also, the treatment of hydrogen as a product is illogical. Burning of  $\text{CH}_{0.686}\text{O}_{0.32}$  presented by (3.81) does not give  $\text{H}_2$  as a product!

We think that the reaction



which represents a correct version of (3.81) is very interesting for chemistry.

From (3.82) one obtains this scheme

	$\text{CH}_{0.686}\text{O}_{0.32}$	$\text{O}_2$	$\text{N}_2$	$\text{CO}$	$\text{CO}_2$	$\text{H}_2\text{O}$	$\text{CH}_4$	$\text{N}_2\text{O}_3$
C	1	0	0	-1	-1	0	-1	0
H	0.686	0	0	0	0	-2	-4	0
O	0.32	2	0	-1	-2	-1	0	-3
N	0	0	2	0	0	0	0	-2

Reaction matrix  $A$  of (3.82) has this form

$$A = \begin{bmatrix} 1.000 & 0 & 0 & -1 & -1 & 0 & -1 & 0 \\ 0.686 & 0 & 0 & 0 & 0 & -2 & -4 & 0 \\ 0.320 & 2 & 0 & -1 & -2 & -1 & 0 & -3 \\ 0.000 & 0 & 2 & 0 & 0 & 0 & 0 & -2 \end{bmatrix}$$

The reaction (3.82) reduces to the following system of linear equations

$$\begin{aligned} x_1 &= x_4 + x_5 + x_7, \\ 0.686 x_1 &= 2 x_6 + 4 x_7, \\ 0.32 x_1 + 2 x_2 &= x_4 + 2 x_5 + x_6 + 3 x_8, \\ 2 x_3 &= 2 x_8. \end{aligned} \quad (3.83)$$

The general solution of the system (3.83) is

$$\begin{aligned} x_5 &= 1.977 x_1/4 + x_2/2 - 3 x_3/4 - 3 x_4/4, \\ x_6 &= -1.337 x_1/2 + x_2 - 3 x_3/2 + x_4/2, \\ x_7 &= 2.023 x_1/4 - x_2/2 + 3 x_3/4 - x_4/4, \\ x_8 &= x_3, \end{aligned} \quad (3.84)$$

where  $x_i > 0$  ( $1 \leq i \leq 4$ ) are arbitrary real numbers.

Since  $x_i > 0$  ( $5 \leq i \leq 8$ ), then from (3.84) one obtains this system of inequalities

$$\begin{aligned} 1.977 x_1 + 2 x_2 - 3 x_3 - 3 x_4 &> 0, \\ -1.337 x_1 + 2 x_2 - 3 x_3 + x_4 &> 0, \\ 2.023 x_1 - 2 x_2 + 3 x_3 - x_4 &> 0. \end{aligned} \quad (3.85)$$

From (3.85) immediately follows this inequality

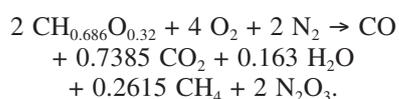
$$1.337 x_1 - x_4 < 2 x_2 - 3 x_3 < 2.023 x_1 - x_4. \quad (3.86)$$

Reaction (3.82) holds if and only if the condition (3.86) is satisfied.

The reaction (3.82) contains three subgenerators which induce a topology of its solutions, but we omitted it, since it will be a subject of the author's next research.

The other particular cases of (3.82) are not considered because we took into account the Remark 3.7.

For instance, for  $x_1 = 2$ ,  $x_2 = 4$ ,  $x_3 = 2$  and  $x_4 = 1$ , from (3.84) one obtains this particular solution  $x_5 = 0.7385$ ,  $x_6 = 0.163$ ,  $x_7 = 0.2615$  and  $x_8 = 2$ . Then (3.82) becomes



Now, we shall determine the minimal coefficients of the reaction (3.82). The Moore–Penrose generalized matrix  $A^+$  will have this form

$$A^+ = \begin{bmatrix} 0.334436538275454 & -0.037800281937753 \\ -0.164755899838609 & 0.019118215665491 \\ 0.123566924878957 & -0.014338661749118 \\ -0.338363333974391 & 0.077822527216911 \\ -0.255985384055086 & 0.068263419384166 \\ 0.257141220018618 & -0.145193039626989 \\ -0.071214743695069 & -0.183886228538830 \\ 0.123566924878957 & -0.014338661749118 \\ -0.048377720464309 & 0.036283290348232 \\ 0.171516759260828 & -0.128637569445621 \\ -0.128637569445621 & 0.346478177084216 \\ -0.003380429711109 & 0.002535322283332 \\ -0.089138809341523 & 0.066854107006142 \\ -0.104876595295905 & 0.078657446471929 \\ 0.044141518588323 & 0.033106138941242 \\ -0.128637569445621 & -0.153521822915784 \end{bmatrix}$$

The reaction (3.82) reduces to the matrix form (3.45), whose general solution is given by the expression (3.46).

For  $\mathbf{a} = (1, 1, 1, 1, 1, 1, 1, 1)^T$ , one obtains

$$\mathbf{x}_{min} = (x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8)^T,$$

where

$$\begin{aligned} x_1 &= 1.241594646560723466, \\ x_2 &= 1.574780831709873263, \\ x_3 &= 0.568914376217595052, \\ x_4 &= 0.721001830633894027, \\ x_5 &= 0.433611414778957395, \\ x_6 &= 0.251904161474584061, \\ x_7 &= 0.086981401147872044, \\ x_8 &= 0.568914376217595052. \end{aligned}$$

## 5 DISCUSSION

We cannot always trust chemical experiments! We cannot always trust mathematics either, for it can mislead us unless we define away the problem area. However, we surely can trust pure logic – no questionable experiments or unusual mathematical operations.

Are they *methods* when somebody can find counterexamples on every step? Obviously, the answer is negative! It is merely a pale picture of the old chemically irrational traditionalism of the past chemistry.

As it is showed by all counterexamples given in this work the traditional procedures for balancing chemical reactions are inconsistent. These particular procedures, we hope that they are the last traditional unsuccessful approach of balancing chemical reactions. Long time ago chemistry lost the battle with mathematics in sense of balancing chemical reactions.

Before we finish this discussion, we would like to stress here, that our facts for arguing are founded by virtue of scientific results.

From current view point of balancing chemical equations, we feel free to tell that traditional approach of balancing chemical reactions is only a history, and Jones' problem<sup>44</sup>, which was as one of the hardest problems of balancing chemical reactions is completely solved<sup>45</sup>.

There exists a completely satisfactory ways of avoiding paradoxes<sup>7,34,45,46,48-50</sup>. The theory used is based on the idea of formal approach of balancing chemical reactions. In these works completely new general highly sophisticated methods are developed for balancing chemical reactions and their stability by virtue of the theory of generalized matrix inverse using Moore–Penrose, Drazin and von Neumann matrices. By these methods chemistry is cleaned from old traditional inconsistent procedures for balancing chemical reactions, such that is open a brand new direction for development of this topic in chemistry and its foundation on genuine principles. That is the newest trend in chemistry about this issue, which showed that traditionalism in chemistry is over.

## 6 CONCLUSION

By this work the consideration of paradoxes in chemistry will begin very seriously as a special object and in any way it will increase researchers' carefulness to avoid the appearance of paradoxes. Sure, no perfect science! Appearance of paradoxes is always possible.

It is more than certain, that this work opened doors for the next research in chemistry for its diagnostic of paradoxes and their resolution. It will accelerate the newest contemporary research in chemistry and it will destroy all barriers which hamper the development of chemistry and lay its foundation on genuine scientific principles.

This work affirms:

- that all formally provable mathematical methods are true if chemical reactions are considered as a consistent formal system,
- that all mathematical truths can be formally provable, and
- that the new branch **Foundation of Chemistry** proves the consistency and completeness of the formal approach of balancing chemical reactions and that it will be a special kind of chemistry, *i.e.*, it will be a finite theory which contains only perfectly well known concepts with true axioms and positive conclusions. It affirms that the principles used in the mathematical approach of balancing chemical reactions, will not lead to contradictions.

After that, what is proven about the paradoxes in this work is there a *general chemistry*? Or it should be refounded on genuine principles as *elementary chemistry*?

The replies to these two questions are looking for deep reform in chemistry in a formalistic way, because in the opposite case paradoxes will be a stumbling block for

a long time. To avoid this awkward position, reforms in chemistry are needed as soon as possible.

Sure, that the above topic is considered in a rough form, but it happens with every pioneer's job.

## ACKNOWLEDGEMENT

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## REFERENCES

- <sup>1</sup> H. B. Curry, *Foundations of Mathematical Logic*, 2<sup>nd</sup> Ed., Dover Pub. Inc., New York 1977, pp. 3–8
- <sup>2</sup> B. R. Gelbaum, J. M. H. Olmsted, *Counterexamples in Analysis*, Dover Pub. Inc., New York 2003
- <sup>3</sup> G. L. Wise, E. B. Hall, *Counterexamples in Probability and Analysis*, Oxford Univ. Press, Oxford 1993
- <sup>4</sup> J. P. Romano, A. F. Siegel, *Counterexamples in Probability and Statistics*, Chapman & Hall, New York – London 1986
- <sup>5</sup> L. A. Steen, J. A. Seebach, Jr., *Counterexamples in Topology*, Dover Pub. Inc., New York 1995
- <sup>6</sup> B. R. Gelbaum, J. M. H. Olmsted, *Theorems and Counterexamples in Mathematics*, Springer Vlg. New York, Inc., New York 1990
- <sup>7</sup> I. B. Risteski, *A new complex vector method for balancing chemical equations*, *Mat. & Technol.* 44 (2010), 193–203
- <sup>8</sup> E. H. Moore, *On the reciprocal of the general algebraic matrix*, *Bull. Amer. Math. Soc.* 26 (1920) 394–395
- <sup>9</sup> R. Penrose, *A generalized inverse for matrices*, *Proc. Cambridge Phil. Soc.* 51 (1955), 406–413
- <sup>10</sup> B. Bunch, *Mathematical Fallacies and Paradoxes*, Van Nostrand, New York 1982, p. 2
- <sup>11</sup> J. W. Oliver, *Formal fallacies and other invalid arguments*, *Mind* 76 (1967), 463–478
- <sup>12</sup> D. H. Sanford, *Contraries and subcontraries*, *Noûs* 2 (1968), 95–96
- <sup>13</sup> E. J. Barbeau, *Mathematical Fallacies, Flaws, and Flimflam*, Math. Assoc. Amer., Washington DC 2000
- <sup>14</sup> C. L. Hamblin, *Fallacies*, Methuen, London 1970, p. 12
- <sup>15</sup> E. A. Maxwell, *Fallacies in Mathematics*, Cambridge Univ. Press, Cambridge 1959, p. 9
- <sup>16</sup> R. M. Sainsbury, *Paradoxes*, 2<sup>nd</sup> Ed., Cambridge Univ. Press, Cambridge 2002, p. 1
- <sup>17</sup> N. Rescher, *Paradoxes: Their Routs, Range and Resolution*, Open Court, Chicago 2001, p. 6
- <sup>18</sup> Ch. S. Chihara, *The semantic paradoxes: A diagnostic investigation*, *Philos. Rev.* 88 (1979), 590–618
- <sup>19</sup> W. V. Quine, *The Ways of Paradoxes*, Harvard Univ. Press, Cambridge Mass. 1966, p. 7
- <sup>20</sup> R. A. Koons, *Paradoxes of Belief and Strategic Rationality*, Cambridge Univ. Press, Cambridge 1992, p. 8
- <sup>21</sup> D. Davidson, *The Prussian blue paradox*, *J. Chem. Educ.* 14 (1937), 238–241
- <sup>22</sup> F. Feigl, *Spot reaction experiments, Part VII: Chemical paradoxes*, *J. Chem. Educ.* 21 (1944), 347–353
- <sup>23</sup> C. Levinthal, *Are there pathways for protein folding?* *J. Chim. Phys.* 65 (1968), 44–45
- <sup>24</sup> C. K. Jørgensen, *Models and paradoxes in quantum chemistry*, *Theor. Chim. Acta* 34 (1974), 189–198
- <sup>25</sup> J. A. Campbell, *Paradigms and paradoxes*, *J. Chem. Educ.* 57 (1980), 41–42

- <sup>26</sup> C. K. Jørgensen, *New paradoxes of spin-pairing energy in gadolinium (III)*, J. Less Common Metals 148 (1989), 147–150
- <sup>27</sup> G. A. Patani, E. J. LaVoie, *Bioisosterism: A rational approach in drug design*, Chem. Rev. 96 (1996), 3147–3176
- <sup>28</sup> D. L. Anderson, *The helium paradoxes*, Proc. Nat. Acad. Sci. USA 95 (1998), 4822–4827
- <sup>29</sup> F. H. Chapple, *The temperature dependence of  $\Delta G^\circ$  and the equilibrium constant,  $K_{eq}$ : Is here a paradox?* J. Chem. Educ. 75 (1998), 342
- <sup>30</sup> E. Vitz, M. J. Schuman, *The  $q/T$  paradox: which 'contains more heat', a cup of coffee at 95°C or a liter of icewater?* J. Chem. Educ. 82 (2005), 856–860
- <sup>31</sup> Ch. G. McCarty, E. Vitz, *pH Paradoxes: demonstrating that it is not true that  $\text{pH} \equiv -\log[\text{H}^+]$* , J. Chem. Educ. 83 (2006), 752–757
- <sup>32</sup> J. M. R. Parrondo, in *EEC HC&M Network on Complexity and Chaos*, ISI, Torino, Italy, 1996, (unpublished)
- <sup>33</sup> D. C. Osipovitch, C. Barratt, P. M. Schwartz, *Systems chemistry and Parrondo's paradox: computational models of thermal cycling*, New J. Chem. 33 (2009), 2022–2027
- <sup>34</sup> I. B. Risteski, *A new pseudoinverse matrix method for balancing chemical equations and their stability*, J. Korean Chem. Soc. 52 (2008), 223–238
- <sup>35</sup> O. F. Steinbach, *Non-stoichiometric equations*, J. Chem. Educ. 21 (1944), 66, 69
- <sup>36</sup> W. T. Hall, *Non-stoichiometric equations*, J. Chem. Educ. 21 (1944), 201–202
- <sup>37</sup> A. Lehrman, *Non-stoichiometric equations*, J. Chem. Educ. 21 (1944), 202–203
- <sup>38</sup> A. Standen, *Some simple balancing*, J. Chem. Educ. 22 (1945), 461–462
- <sup>39</sup> W. C. McGavock, *Non-stoichiometric equations*, J. Chem. Educ. 22 (1945), 269–270
- <sup>40</sup> W. C. McGavock, *Organic Oxidation-Reduction Reactions*, 2<sup>nd</sup> Ed. San Antonio 1945, p. 135
- <sup>41</sup> A. Porges, *A question of balancing*, J. Chem. Educ. 22 (1945), 266–267
- <sup>42</sup> R. Harré, *Some presuppositions in the metaphysics of chemical reactions*, Found. Chem. 10 (2008) 19–38
- <sup>43</sup> E. V. Krishnamurthy, *Generalized matrix inverse for automatic balancing of chemical equations*, Int. J. Math. Educ. Sci. Technol. 9 (1978), 323–328
- <sup>44</sup> M. Jones, *Problem 71–25\*: Balancing chemical equations*, SIAM Rev. 13 (1971), 571
- <sup>45</sup> I. B. Risteski, *A new approach to balancing chemical equations*, SIAM Problems & Solutions, (2007), 1–10
- <sup>46</sup> I. B. Risteski, *The new algebraic criterions to even out the chemical reactions*, 22<sup>nd</sup> Oct. Meeting of Min. & Metall., Collection of Papers, Oct. 1–2, 1990, Bor, 313–318
- <sup>47</sup> K. Gödel, *What is Cantor's continuum problem?* Amer. Math. Monthly 54 (1947), 515–527
- <sup>48</sup> I. B. Risteski, *A new non-singular matrix method for balancing chemical equations and their stability*, Int. J. Math. Manuscripts 1 (2007), 180–205
- <sup>49</sup> I. B. Risteski, *A new generalized matrix inverse method for balancing chemical equations and their stability*, Bol. Soc. Quím. Méx. 2 (2008), 104–115
- <sup>50</sup> I. B. Risteski, *A new singular matrix method for balancing chemical equations and their stability*, J. Chin. Chem. Soc. 56 (2009), 65–79
- <sup>51</sup> G. R. Blakley, *Chemical equations balancing*, J. Chem Educ. 59 (1982), 728–734
- <sup>52</sup> S. C. Das, *A mathematical method of balancing a chemical equation*, Int. J. Math. Educ. Sci. Technol. 17 (1986), 191–200
- <sup>53</sup> A. García, *A new method to balance chemical equations*, J. Chem Educ. 64 (1987), 247–248
- <sup>54</sup> V. M. Petruševski, *A fast solution to the problem of balancing redox equations: Numbers introducing formal balance*, Glas. hem. tehnol. Makedonija 17 (1998), 141–145
- <sup>55</sup> Z. Tóth, *On balancing 'redox challenges' by unconventional oxidation numbers*, J. Chem. Educ. 74 (1997), 1270
- <sup>56</sup> O. Ludwig, *Balancing chemical equations*, J. Chem. Educ. 74 (1997), 1270–1271
- <sup>57</sup> M. J. ten Hoor, *Chemical equations with a non-unique balance*, Chem NZ 105 (2006), 7–10
- <sup>58</sup> A. F. Holleman, E. Wiberg, *Inorganic Chemistry*, Academic Press, Berlin – New York 2001, pp. 810–811
- <sup>59</sup> J. Croteau, W. P. Fox, K. Varazo, *Mathematical modeling of chemical stoichiometry*, PRIMUS 17 (2007), 301–315
- <sup>60</sup> M. V. Ramanan, E. Lakshmanan, R. Sethumadhavan, S. Renganaayanan, *Performance prediction and validation of equilibrium modeling for gasification of cashew nut shell char*, Braz. J. Chem. Eng. 25 (2008), 585–601