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THE STOICHIOMETRIC UNIQUENESS OF MULTIPLE CHEMICAL REACTION SYSTEMS IN CHEMICAL THERMODYNAMICS, KINETICS AND CATALYSIS – CONTRIBUTIONS OF PROFESSOR ILIE FISHTIK

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Abstract. The main scientific achievements of great significance accomplished by Professor Ilie Fishtik at the University of Iowa and the Worcester Polytechnic Institute, in several fields of the physical chemistry as chemical thermodynamics, kinetics and heterogeneous catalysis were revealed and briefly analyzed. Fundamental equations of chemical thermodynamics within the De Donder (stoichiometric) approach were reformulated in terms of a special class of chemical reactions, called as response reactions. Using this approach, the unusual behavior of chemical equilibrium systems, to interpret the apparent contradictions to Le Chatelier principle and to discover hitherto unnoticed thermodynamic identities, was rationalized. The stabilities of chemical species were formulated in terms of a certain class of stoichiometrically unique chemical reactions and their thermochemical characteristics. A completely new approach for the generation and simplification of kinetic mechanisms for complex reaction systems was developed and applied. Based on a new type of reaction networks, referred to as reaction route graphs, a systematic method of analysis and reduction of a microkinetic mechanism was established and employed.

Keywords: response reaction, chemical thermodynamics, kinetics, heterogeneous catalysis, stoichiometry.

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List of abbreviations:

ER	elementary reaction
GA	group additivity
IR	intermediate reaction
OLS	ordinary least squares
OR	overall reaction
QSS	quasi-steady state
RER	response reaction
RR	reaction route
SIR	stoichiometrically independent reaction
TOF	turn-over frequency

Introduction

This work presents the use of Professor Fishtik's concept of the stoichiometric uniqueness of multiple chemical reaction systems in different fields of physical chemistry.

The references of this paper contain the scientific publications of Professor Fishtik except for the papers published in the conference collections during the years 1975-1996, in the chronological order, starting with the most recent ones [1-154].

The aim of this paper is to succinctly analyze the main accomplishments of the research activities of Professor Ilie Fishtik outside the Republic of Moldova, at the Department of Chemical and Biochemical Engineering of the University of Iowa and the Department of Chemical Engineering of the Worcester Polytechnic Institute in the U.S.A. [1-85]. References to this paper contain as well the extended list of scientific publications of Professor Fishtik, since 1979.

Background

In this section, Professor Fishtik's most important achievements in the fields of thermodynamics, thermochemistry, kinetics and heterogeneous catalysis will be briefly presented.

1. Response Reactions in Chemical Thermodynamics

Professor Ilie Fishtik showed that the fundamental equations of chemical thermodynamics within the De Donder (stoichiometric) approach may be reformulated in terms of a special class of chemical reactions, called response reactions (RERs) [66,67]. The RERs have the remarkable property of being independent of the actual choice of the stoichiometrically independent reactions, by means of which the chemical process in the system considered is usually described. The concept of RERs was shown to be applicable in both equilibrium and non-equilibrium chemical thermodynamics [57,60,74,81,82,86,87,91,94,95, 100]. This approach enables one to overcome some difficulties and ambiguities of the standard thermodynamic description of complex chemical systems. In particular, the concept of thermodynamic coupling of chemical reactions may be given a new qualitative and quantitative meaning. Using the RERs approach, Professor Fishtik was able to rationalize unusual behavior of chemical equilibrium systems, to interpret the apparent contradictions to Le Chatelier principle and to discover hitherto unnoticed thermodynamic identities.

In a series of papers the main relations of both equilibrium and non-equilibrium chemical thermodynamics in terms of response reactions were analyzed [66,67]. Firstly, a closed system, in which n chemical species $B_1, B_2, ..., B_n$, was considered to interact in accordance with the following complete set of stoichiometrically independent reactions (SIRs):

$$\begin{aligned} &\nu_{11}B_1 + \nu_{12}B_2 + ... + \nu_{1n}B_n = 0 \\ &\nu_{21}B_1 + \nu_{22}B_2 + ... + \nu_{1n}B_n = 0 \\ &.................................... \\ &\nu_{m1}B_1 + \nu_{m2}B_2 + ... + \nu_{mn}B_n = 0 \end{aligned} \qquad (1)$$

i.e., $\nu\left\|B_1, B_2, ...B_n\right\|^t = 0$

where, $$\nu = \begin{Vmatrix} \nu_{11} & \nu_{12} & ... & \nu_{1n} \\ \nu_{21} & \nu_{22} & ... & \nu_{2n} \\ \vdots & \vdots & ... & \vdots \\ \nu_{m1} & \nu_{m2} & ... & \nu_{mn} \end{Vmatrix}$$

is the stoichiometric matrix. In the above formula, as well as later on, the superscript t indicates transposition. The independence of the reactions Eq.(1) is guaranteed by the condition

rank $\upsilon = m$

Each of reactions Eq.(1) is characterized by its extent ξ_j and affinity A_j, which are defined as

$$\delta n_S = \sum_{j=1}^{m} \nu_{jS}\delta\xi_j; \quad s = 1,2,...,n$$

$$A_j = -\sum_{s=1}^{n} \nu_{jS}\mu_S; \quad j = 1,2,...,m$$

Here, n_S and μ_s are the actual number of moles and chemical potential of the species B_s. Let Z be a thermodynamic potential (characteristic function), determined by two physical variables X and Y. In chemical thermodynamics it is habitual to choose the pair X, Y as $S, V; S, P; T, V$ or T, P, in which case Z is respectively the internal energy (U), enthalpy (H), Helmholtz energy (F) and Gibbs energy (G). A closed chemical system may be described either in terms of $Z(X, Y, n_1, n_2, . . . , n_n)$ or in terms of $Z(X, Y, \xi_1, \xi_2, ... , \xi_m)$. In the above cited papers, mainly the latter case was considered, which was referred to as the standard (De Donder or stoichiometric) approach. Since only chemical processes were of interest, the variables X and Y were kept constant. In that case

$$\delta Z_{X,Y} = \sum_{j=1}^{m}\left(\frac{\partial Z}{\partial \xi_j}\right)\delta\xi_j = -\sum_{j=1}^{m} A_j\delta\xi_j \qquad (2)$$

For every thermodynamic potential the following two matrices can be defined

$$Z = \left\|Z_{rs}\right\|; \quad Z_{rs} = \frac{\partial^2 Z}{\partial\xi_r\partial\xi_s} = \sum_{k=1}^{n}\nu_{rk}\frac{\partial\mu k}{\partial\xi_s} \qquad (3)$$
$$r, s = 1,2,...m$$

$$R = \left\|R_{rs}\right\|; \quad R_{rs} = \frac{\partial^2 Z}{\partial n_r\partial n_s} = \frac{\partial\mu_r}{\partial n_s} \qquad (4)$$
$$r, s = 1,2,...n$$

These matrices are interrelated as

$$Z = \upsilon R \upsilon^t \qquad (5)$$

The determinant of the Hessian matrix, Z, Eq.(3), is denoted by Δ:

$$\Delta = \begin{Vmatrix} Z_{11} & Z_{12} & ... & Z_{1n} \\ Z_{21} & Z_{22} & ... & Z_{2n} \\ \vdots & \vdots & ... & \vdots \\ Z_{m1} & Z_{m2} & ... & Z_{mn} \end{Vmatrix} \qquad (6)$$

This determinant is necessarily a positive value and is called the Hessian determinant.

Two definitions and main properties of RERs were formulated [66,67] as followed. It was supposed a set of stoichiometrically independent reactions is given by Eq.(1). Further, it was supposed that $i_1, i_2, . . , i_{m-1}$, are integers, satisfying the conditions

$$1 < i_1 < i_2 < ... < i_{m-1} < n \qquad (7)$$

Definition *a*. The stoichiometric relation given by Eq.(8) is a response reaction (RER):

$$\sum_{i=1}^{n} \nu_i B_i = 0 \qquad (8)$$

where,

$$\nu_i = \nu_i(R) = \begin{Vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \nu_{1,i_{m-1}} & \nu_{1i} \\ \nu_{2,i_1} & \nu_{2,i_2} & \nu_{2,i_{m-1}} & \nu_{2i} \\ \vdots & \vdots & \cdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \nu_{m,i_{m-1}} & \nu_{mi} \end{Vmatrix} \qquad (9)$$

The response reactions specified by Eqs.(8,9) were denoted as $R = R(i_1, i_2, \ldots, i_{m-1})$.

Definition *b*. Each (*m-1*)-tuple of integers i_1, i_2, . . . , i_{m-1}, satisfying the conditions in Eq.(7), determines a response reaction. The following expressions can be immediately deduced from definitions ***a*** and ***b***.

The number of RERs is equal to $M = \binom{n}{m-1}$.

The indices i_1, i_2, . . . , i_{m-1} correspond to the respective columns of the stoichiometric matrix υ, *i.e.*, to the chemical species

$B_{i_1}, B_{i_2}, \ldots, B_{i_{m-1}}$.

Thus, a RER may be defined by *m-1* species

$B_{i_1}, B_{i_2}, \ldots, B_{i_{m-1}}$

every time when $i = i_l$ or $i = i_2$, or . . . $i = i_{m-1}$ two columns of the determinant on of Eq.(9) are equal. Consequently, in $R(i_1, i_2, , . . . , i_{m-1})$ the species

$B_{i_1}, B_{i_2}, \ldots, B_{i_{m-1}}$

have zero stoichiometric coefficients and, hence, are not involved in this particular RER.

The main result could be formulated by the following Eqs.(10,11):

$$\delta Z_{X,Y} = \sum_{R}\sum_{R'} L(R,R')A(R)\delta A(R') \qquad (10)$$

$$\delta^2 Z_{X,Y} = \sum_{R}\sum_{R'} L(R,R')\delta A(R)\delta A(R') \qquad (11)$$

where, *R* and *R'* are two RERs and *L* is the coupling coefficient:

$$L(R,R') = \frac{1}{\Delta}\begin{Vmatrix} R_{i_1,j_1} & R_{i_1,j_2} & \cdots & R_{i_1,j_{m-1}} \\ R_{i_2,j_1} & R_{i_2,j_2} & \cdots & R_{i_2,j_{m-1}} \\ \vdots & \vdots & \cdots & \vdots \\ R_{i_{m-1},j_1} & R_{i_{m-1},j_2} & \cdots & R_{i_{m-1},j_{m-1}} \end{Vmatrix} \qquad (12)$$

L(*R,R'*) is associated with the coupling between response reactions *R* and *R'*.

The results stated above show that the fundamental equations of chemical thermodynamics may be transformed so as to contain a sum of contributions coming from RERs and pairs thereof. In chemical thermodynamics the pairs of physical variables *X* and *Y* are usually equal to *S, V; S, P; T, V* or *T, P*. For these choices, within the standard stoichiometric approach, it follows:

$$\delta U = T\delta S - P\delta V - \sum_{j=1}^{m} A_j \delta\xi_j$$

$$\delta H = T\delta S + V\delta P - \sum_{j=1}^{m} A_j \delta\xi_j$$

$$\delta F = -S\delta T - P\delta V - \sum_{j=1}^{m} A_j \delta\xi_j$$

$$\delta G = -S\delta T + V\delta P - \sum_{j=1}^{m} A_j \delta\xi_j$$

By means of Eq.(10) the last terms in these fundamental equations may be presented as sums of contributions coming from RERs:

$$\delta U = T\delta S - P\delta V + \sum_{R}\sum_{R'} L(R,R')_{S,V} A(R)\delta A(R')_{S,V}$$

$$\delta H = T\delta S + V\delta P \sum_{R}\sum_{R'} L(R,R')_{S,P} A(R)\delta A(R')_{S,P}$$

$$\delta F = -S\delta T - P\delta V \sum_{R}\sum_{R'} L(R,R')_{T,V} A(R)\delta A(R')_{T,V}$$

$$\delta G = -S\delta T + V\delta P \sum_{R}\sum_{R'} L(R,R')_{T,P} A(R)\delta A(R')_{T,P}$$

This approach was referred to as the RER-approach. A comparison between the standard and the RER- approaches reveals that the difference between them is fundamental. First, instead of a set of independent extensive variables ξ_1, ξ_2, . . . , ξ_m a set of dependent intensive variables *A(R)* is used. In other words, the functional dependence $Z(X, Y, \xi_1, \xi_2, \ldots, \xi_m$ is transformed into $Z[X, Y, A(1), A(2), \ldots, A(M)]$.

The Eq.(10) can be written in a different form:

$$\delta Z_{X,Y} = \sum_{R} \Omega(R)\delta A(R)$$

where

$$\Omega(R) = \sum_{R'} L(R,R')A(R')$$

With this notation the fundamental equations of chemical thermodynamics are written in a more traditional way as:

$$\delta U = T\delta S - P\delta V + \sum_R \Omega(R)_{S,V}\delta A(R)_{S,V}$$

$$\delta H = T\delta S + V\delta P + \sum_R \Omega(R)_{S,P}\delta A(R)_{S,P}$$

$$\delta F = -S\delta T - P\delta V + \sum_R \Omega(R)_{T,V}\delta A(R)_{T,V}$$

$$\delta G = -S\delta T + V\delta P + \sum_R \Omega(R)_{T,P}\delta A(R)_{T,P}$$

Thus, within the RER-approach *Ω(R)* plays the role of the generalized force whereas *A(R)* is the generalized coordinate. Notice that the force *Ω(R)* is an extensive, while the coordinate *A(R)* is an intensive quantity. The second important difference between the standard and the RER-approach is that in the latter, the fundamental thermodynamic equations are given in terms of the quantities *L*(*R,R'*) defined by Eq.(12). At last, the most remarkable difference between the standard and the RER-approach is that within the RER-approach the fundamental thermodynamic equations become absolutely independent on the (starting) choice of SIRs. Therefore, instead of an infinite number of different (yet equivalent) fundamental thermodynamic equations within the standard approach, one has a single such equation. By this, the independence of the results of chemical thermodynamics from the choice of SIRs become evident. It was concluded the RER-approach is just a transformation of the fundamental thermodynamic equations from one basis (an arbitrary set of SIRs) to another one (response reactions).

A new approach to the evaluation of stability of chemical species was initiated and developed in [40,47]. The main clue was to permit the species to abstractly interact *via* a special type of chemical reaction so that an equilibrium state was reached. In addition, the energies of the species were allowed to vary from their initial (standard) to their equilibrium values so that the energy change of any conceivable reaction at equilibrium was equal to zero. The equilibrium energies of the species were supplementary estimated by an optimization procedure analogous to that of the least squares method. A species was considered unstable if the difference between its initial and equilibrium energy was positive (the species releases energy). On the contrary, if the difference between the initial and the equilibrium energy of a species was negative, the species was stable (the species absorbed energy). This type of stability of species was referred to as the overall stability. Using the response reactions (RERs) formalism, one showed further that the overall stabilities of the species may be partitioned into different types of contributions [71,86,87,91,94,95]. Specifically, it was proved that the conventional definition of stability of the species was just an appropriately normalized part of the overall stability. The relative stabilities of a given class of species were normally evaluated on the basis of stoichiometric and thermochemical considerations. In particular, one of the simplest and most often employed procedures was as follows. First, an appropriate set of reference species was selected. Next, a certain type of reaction including each test species and reference species, accompanied by their energy (enthalpy) changes, was generated. As a final point, the energy (enthalpy) changes of the reactions were normalized to a common characteristic of the test species, *e.g.*, energy (enthalpy) change of the reaction per atom, per mole, per ring, per *π* electron, *etc*. In many cases, the assessment of the relative stabilities of the species engaging the procedure concisely defined above gave accurate results. There were cases, however, when the predicted relative stabilities of the species were wholly mistaken.

Professor Fishtik proposed a new rigorous definition, an algorithm of evaluation, and a remarkable interpretation of the stability of chemical species. In addition, an analytical equation for the stability, was derived that explicitly related the thermochemical and stoichiometric characteristics of the species. The approach is general and valid for any type of stability [40,47]. The main feature of this general result was a distinct interpretation of the stability. As a consequence, the stabilities of chemical species can be always formulated in terms of a certain class of stoichiometrically unique chemical reactions and their thermochemical characteristics [5,8,27,34,40,41,47,59,95]. This interpretation also reveals that several types of stabilities of species may be imagined and defined. Specifically, in a system containing an assumed set of reference and test species one can define and assess the overall stabilities of the species. This type of stability is the most complete because it takes into account all possible contributions coming from both reference and test species. The overall stabilities may be further decomposed into relative and direct stabilities. Clearly, the most useful and physically sensitive type of stability is the relative stability, *i.e.*, the stability of a given species with respect to a certain set of reference species. As shown, the relative stability of species is closely related to the conventional stability [47]. Simultaneously, the conventional stability, as distinct from the relative stability defined in [47], is not appropriately normalized. As a consequence, in many cases the conventional stabilities of the species are mistaken. Specifically, it was shown that such thermodynamic and stoichiometric relations could be uniquely partitioned into a sum of contributions associated with a special class of reactions, referred to as response reactions (RERs). Additionally, the equation for the change of Gibbs energy in complex chemical systems was reformulated in terms of the considered RERs. The present formulation has the remarkable property of being unique: the composition of the species unambiguously determines the response reactions and *via* them the change of the Gibbs energy of the system. Moreover, it enables one to reinterpret and explain some basic concepts of chemical thermodynamics, as coupling between reactions, sensitivity coefficients, etc. The above considerations show that there exists a unique stoichiometric representation in the chemical thermodynamics of multiple reactions. In other words, the arbitrary stoichiometrically independent reactions (SIRs) can always be transformed into the unique RERs. The transformation of the fundamental equations of chemical thermodynamics, from a SIR-basis to the RERs, envisages new, previously unnoticed, structures of these equations. This has two consequences. First, the controversial concept of thermodynamic coupling may be interpreted in a new qualitative and quantitative manner. In terms of RERs the coupling appears in a natural way and is given explicitly. Second, the substitution of extents of reactions as independent variables by affinities, implies that in non-equilibrium thermodynamics the role of flux is played by the rate of change of affinities, instead by the rate of change of extents of reactions. By this, insufficiencies due to different transformation rules for the forces and fluxes in non-equilibrium systems are automatically eliminated. An important advantage of the developed approach in terms of RERs, compared to the standard approach (in terms of SIRs), is that the sensitivity coefficients, characterizing the response of an equilibrium system to the change of different parameters governing its position, may be decomposed into sums of terms, uniquely assigned to individual RERs [47].

A general thermodynamic and stoichiometric method, developed by Fishtik, I. and Datta, R. [47], to study subtle forms of stability/instability relations among chemical species, such as resonance and strain energies, was extended to stability relations in multiple chemical reaction systems [40]. A new definition as well as a new algorithm of evaluation of the stabilities of chemical species, referred to as the overall stabilities, was proposed. It was shown that the overall stabilities may be partitioned into a sum of contributions associated with a complete set of stoichiometrically unique response reactions (RERs). This finding reveals that the conventional stability analysis is stoichiometrically and thermodynamically inconsistent in that it involves only a part of RERs. This approach not only provides a remarkable interpretation and an algorithm for evaluation of the species stabilities but also clearly shows the limitations and thermodynamic inconsistency of the conventional graphical methods of stability analysis. In the work [40] the stability relations among chemical species are considered exclusively in terms of the stoichiometric approach to the chemical equilibrium, *i.e.*, the approach based on the substitution of the mass balance conditions with an arbitrary set of chemical reactions. It is well-known that the evaluation of different types of stabilities among chemical species may be performed only employing concomitantly thermodynamic and stoichiometric considerations. Habitually, the stability relations in multiple chemical reaction systems are studied employing graphical methods by evaluating and plotting the stability restrictions of chemical species. The stability boundaries are conventionally determined from the equilibrium conditions of single reactions. In fact, this approach is equivalent to a combinatorial partition of a multiple chemical reaction system into several one-reaction subsystems. Each of these one-reaction subsystems is analyzed separately; *i.e.*, it is implicitly supposed that the overall equilibrium conditions in a multiple chemical reaction system may be substituted with a set of equilibrium conditions of individual one-reaction subsystems. Evidently, this approach disrupts the equilibrium conditions in a multiple chemical reaction system, in that, at equilibrium, the Gibbs free-energy change of any possible reaction should be equal to zero. In [40] the Professor Fishtik addressed the problem of stability of chemical species in multiple chemical reaction systems from a different point of view. This approach is based on a quantity that is directly related to the stability of chemical species. The function, referred to as the overall stability, is just the change in the partial Gibbs free energy of the species when the system is moving from a given initial state to an equilibrium state. The overall stabilities of species are evaluated by combining the usual thermodynamic and stoichiometric formalism with the least-squares method. Therefore, the overall stability approach warrants rigorous equilibrium conditions of the whole system at any point in the variable space. It was also shown that the overall stabilities have a remarkable physicochemical meaning. More explicitly, the overall stabilities may be partitioned into a sum of contributions associated with a unique set of RERs. In this way, the overall stability of the species may be considered as an exact, complete, and unique thermodynamic and stoichiometric balance in the system.

Thermodynamic analysis is a valuable and powerful tool in predicting, comprehending, and rationalizing the stability relations in redox reaction systems [34,40,42,128,130]. To simplify the treatment and, at the same time, enhance the visual factor, the stability relations are often analyzed employing graphical methods, *i.e.*, by plotting the stability fields of chemical species as a function of the variables that determine the position of the electrochemical equilibrium. On the overall level, as well-known, conventional chemical thermodynamics itself does not provide a means to select a set of reactions out of an infinity of allowed sets. Stability relations in multiple redox reaction systems comprising one element are predictably generated on the basis of the thermodynamic analysis of a certain class of reactions involving in a combinatorial manner all pairs of species included in the system. This indicates that the stability relations in a complex system are additive in that the stability relations may be partitioned into a linear sum of contributions coming from individual redox reactions. These reactions are stoichiometrically unique and are identical to RERs, deduced from chemical thermodynamics. Adopting a new quantitative definition of the stability of the species referred to as the overall stability and employing the concept of stoichiometric uniqueness in a complex chemical reaction system, author [34,40] shown that stability relations may be certainly partitioned into a sum of contributions coming from RERs. Therefore, one arrives at an exact and stoichiometrically unique formulation of stability relations in multiple chemical reaction systems. This new fundamental result leads to a simple and thermodynamically rigorous principle in constructing overall Pourbaix diagrams. Concomitantly, the developed overall stability approach allowed a deeper insight into the main assumptions of the conventional stability analysis in electrochemical systems. As well-known, according to the conventional approach a species is stable if the Gibbs free energies of all reactions involving this particular species are strictly negative. For systems in which the number of atoms of the element M is equal to one in every species comprising the system, the overall and conventional Pourbaix diagrams coincide. If, at least, in one species the number of atoms of the element M is different from one, the two types of Pourbaix diagram may differ. From the detailed analysis presented in [34] it follows that both the conventional and overall stability analyses employ essentially the same set of reactions, *i.e.*, RERs. The two approaches, however, differ in defining the stability field of a species. In this respect, the conventional approach may be regarded as more qualitative in that the absolute values of the Gibbs free energies of the RERs are not important. Thus, if the Gibbs free energy of at least one RER is not favorable toward the formation of a given species, the species is considered unstable regardless of the values of the Gibbs free energies of the remaining RERs. On the contrary, within the overall stability approach, a species may be stable even if the Gibbs free energies of some RERs are thermodynamically not favorable toward the production of this species provided the Gibbs free energies of the remaining RERs may overcome the deficit in Gibbs free energy. As a result, overall stability analysis provides a quantitative and thermodynamically meaningful criterion for generating the predominance lines and triple points.

2. Response Reactions in Chemical Kinetics and Heterogeneous Catalysis

2.1 Theory of Reaction Routes

Reaction charts are commonly used to describe reaction paths in chemistry and cellular biology, and are precious in the research of reaction mechanisms. Usually, species, often displaying molecular structure, are drawn and interrelated by means of arrows to display the reactions. Such a scheme, while suitable for monomolecular reactions, becomes difficult when more than one species participates in a reaction and specially when there are parallel paths. The term “reaction graphs” in the literature refers to the topology of reaction mechanisms and comes from the fact that reaction charts are structurally analogous to graphs, with nodes or vertices signifying species, and branches or edges demonstrating their reactions. The graph theoretical standpoint of mechanisms, in addition to its intuitive application, permits the results of graph theory to be applied for depicting reaction topology, and is mainly useful for computer-assisted recording. The key use of chemical graph theory is in the study of molecular structure; nevertheless, it is being progressively used in the interpretation of reaction mechanisms. Graph methods were used broadly to solve a variety of topological problems in chemistry, including the topological description of complex chemical reaction networks. More recently, complex biochemical networks were discussed within a rather general mathematical network theory. A universal characteristic of the graph-theoretical approach used for the topological description of chemical reaction networks was that each node, or vertex, represented a single species, while the branches, or edges, represented the species connectivity consistent with the elementary reaction steps encompassing the mechanism. Although the notion of correlating the species with the nodes is remarkable (being equivalent to the conventional way of describing mechanisms in chemistry) and is a useful formalism for studying monomolecular reaction networks, this method cannot be drawn-out to the more general cases and leaves open a series of fundamental problems concerning complex chemical mechanisms. For example, the conventional reaction graphs cannot, in general, be used in a straightforward manner for kinetic analysis, reduction, and simplification. It was shown that this new type of graph represents a powerful tool in studying complex, nonlinear kinetic mechanisms. Another key advantage of the RR graph approach is that there exists a direct analogy between the RR graphs and electrical networks, which provides a powerful new set of tools for kinetic analysis, including Kirchhoff's laws.

The concept of a Kirchhoff graph comes out of the chemical reaction network theory. As the name implies, when based on a reaction network, a Kirchhoff graph satisfies both the Kirchhoff current law and the Kirchhoff potential law, and is therefore a circuit diagram for that reaction network. Their role in this context was discussed by Fishtik, I., Datta, R. *et al.* [26,45,49,50,73] and in some of their references. In the latter works, Kirchhoff graphs are referred to as reaction route graphs. The concept of a Kirchhoff graph thus connects the fundamental theorem of linear algebra with the fundamental conservation principle in the Kirchhoff laws. There is also the important and distinct concept of a Kirchhoff or Laplacian matrix and the well-known Kirchhoff theorem which relates the eigenvalues of the Kirchhoff matrix for a graph to the number of spanning trees of that graph.

A new graph-theoretical approach was developed [41,49,50] that overcame many of the limitations of the existed methodologies and could be a great tool in the graphical picture, along with mechanistic and kinetic elucidation of reaction networks based on reaction route theory and their analogy with electrical circuits. The "reaction route graphs" were different from "reaction graphs" because the nodes did not represent a certain species but, somewhat simply show how the elementary steps, or graph branches, are linked to describe different reaction routes [1,12,16,17,21,24,26,30,43,45,48-50,67,72,73,78].

The reaction route network was interpreting as a ramble through a mountain group with many crests and valleys that matched individual elementary reaction steps. Within the transition-state theory, the valleys were regarded abstractly as the energy level of reactants or products, while a single elementary reaction was interpreted as the trek from one valley to a neighboring one over a mountain pass, illustrative of the energy barrier for a unit reaction. Many such trips constitute the total hike and are related to the reaction route network for an overall reaction. Consequently, an infinite diversity of reaction routes (RRs) occurs, in principle, for a given hike in transiting from the reactants to the products, including those involving loops or cycles, which were presented empty routes (ERs). The direct RRs were defined as the shortest, without any cycles, and were finite in number, although this could be a big one. The depiction of a RR graph, even deprived of a subsequent kinetic analysis, offered a great picturing tool and a profounder understanding of the reaction mechanism, in comparison with the traditional and computationally expensive analyses. An additional use of the electrical circuit analogy and Kirchhoff's laws provides a powerful tool for a quantitative analysis and reduction of the RR network. Evidently, not all of the possible RRs are similarly significant. There were, in fact, many alternative methods accessible for the reduction of kinetic systems. Professor Fishtik proposed a different methodology grounded on the notion of reaction resistance similarly to Ohm's Law, using the techniques of electrical network analysis, to investigate and diminish RR networks. This permitted not only to distinguish among the various RRs, but also to define the slow (or rate-determining) steps, and the quasi-equilibrium steps and, finally, when possible, the derivation of a simple and accurate algebraic rate equation appropriate for reactor analysis and scheme. The theoretical approach in the case of a single overall reaction characterized by minimal kinetic mechanisms (unit stoichiometric numbers) was developed in [50] followed by its application to heterogeneous and enzyme catalytic reactions [49]. The concept of reaction route (RR) graphs for kinetic mechanisms that produced minimal graphs was extended to the problem of non-minimal kinetic mechanisms in the case of a single overall reaction (OR) [41]. A RR graph was considered minimal if all of the stoichiometric numbers in all direct RRs of the mechanism were equal to ±1 and non-minimal if at least one stoichiometric number in a direct RR was non-unity, *e.g.*, equal to ±2. For an assumed mechanism, four unique topological characteristics of RR graphs were demarcated and numbered, *i.e.*, direct full routes (FRs), empty routes (ERs), intermediate nodes (INs), and terminal nodes (TNs). These were further used to build the RR graphs. One algorithm contains watching each IN as a central node in a RR sub-graph. Consequently, the construction and numbering RR graphs consisted in balancing the peripheral nodes in the RR sub-graphs according to the list of FRs, ERs, INs, and TNs. An alternative method used an independent set of RRs to build the RR graph with adequate the INs and TNs.

The classical theory of reaction routes was revealed to be intimately related to the RERs formalism [16,17,21,26,41,45,48-50]. Namely, starting from general thermodynamic relations, the basic kinetic equation was shown to be identically transformed so, as to be partitioned into a sum of contributions originating from RERs. Each of the RER is produced by a linear combination of the elementary reactions that is nothing but a reaction route. When the intermediate species are assumed to obey the quasi-steady approximation, the contributions coming from RERs involving intermediate species vanish. As a result, the basic kinetic equation could be presented as a sum of contributions coming from RERs involving only reactants and products. This approach was shown to provide an adequate physicochemical basis of reaction routes as well as an effective algorithm of their enumeration. Depending on the type of overall reactions produced by the reaction routes one can distinguish between two distinct types of reaction routes. Thus, one option is to define a reaction route by specifying the intermediate species that need to be eliminated. This type of reaction routes was referred to as Milner reaction routes. The other option is to require the reaction routes to produce RERs thus resulting in reaction routes referred to as Happel-Sellers reaction routes.

The detailed mechanism of the process in the general case of a reacting multiple chemical reaction system comprising n chemical species B_1, B_2,...,B_n was described by the following set of p elementary reactions [48]:

$$r_j = \sum_{i=1}^{n} v_{ji} B_i = 0; \quad j = 1,2,..., p \tag{13}$$

Here υ_{ji} are the stoichiometric coefficients of the species assumed as usual to take positive values for products and negative for reactants. The rank of the stoichiometric matrix υ is

$$rank\ \ v = rank \begin{bmatrix} v_{11} & v_{12} & ... & v_{1n} \\ v_{21} & v_{22} & ... & v_{2n} \\ \vdots & \vdots & ... & \vdots \\ v_{p1} & v_{p2} & ... & v_{pn} \end{bmatrix} = m \le p \tag{14}$$

and, therefore, the elementary reactions are not necessarily linearly independent. A linear combination of the elementary reactions $r_1;r_2;...;r_p$ that eliminated a specified number of species was called a reaction route (RR) and was denoted by R. In the most general case, an RR may be expressed as

$$R = \sum_{j=1}^{p} \sigma_j r_j \tag{15}$$

where, $\sigma_1;\ \sigma_2;...;\ \sigma_p$ is a set of real numbers, called stoichiometric numbers. An RR produces a new reaction that is referred to as an overall reaction (OR). The OR produced by an RR may be obtained by substituting Eq.(13) into Eq.(15):

$$\rho = \sum_{j=1}^{p} \sum_{i=1}^{n} \sigma_j v_{ij} B_i = 0 \tag{16}$$

An RR producing an OR in which all of the stoichiometric coefficients are equal to zero, the so-called “zero” OR, is called a cycle or an empty route (ER). Finally, one should mention that two RRs R_1 and R_2 that differ by a constant γ, *i.e.*,

$R_1 = \gamma R_2$ are considered to be equivalent. Obviously, a particular type of RR may be defined, generated, and enumerated by specifying two major characteristics of the RRs, that is, (1) the number of elementary reactions involved in an RR, and (2) the species that need to be eliminated, or, otherwise, the species that are involved in the produced OR. If these two main characteristics of the RRs are not specified simultaneously, then the RRs along with the corresponding ORs may be derived in an arbitrary manner, *i.e.*, in an infinite number of ways. The arbitrariness of RRs, however, may be overcome if it is required that the number of elementary reactions involved in RR be minimal. By "minimal" is meant that if an elementary reaction is omitted from the RR, then there is no way to eliminate the specified number of species by linearly combining the remaining elementary reactions. An RR that involves a minimal number of elementary reactions in the sense described above is called a direct RR. In order to derive the general formula for a direct RR, it was necessary to partition both the set of elementary reactions $\{r_1;r_2;...;r_p\}$ and the set of species $\{B_1, B_2, ..., B_n\}$ into two subsets. Thus, the set of elementary reactions is partitioned into a subset of *q+1* elementary reactions $\{r_{i_1}, r_{i_2}, ..., r_{j_q}, r_{j_{q+1}}\}(1 \le j_1 < j_2 < ... < j_q < j_{q+1} \le p)$ that *are involved* in a direct RR and a subset of *n-q-1* elementary reactions $\{r_{l_1}, r_{l_2}, ..., r_{l_{p-q-1}}\}(1 \le l_1 < l_2 < ... < l_{p-q-1} \le p)$ that *are not involved* in a direct RR. Here $\{j_1, j_2, ..., j_q, j_{q+1}\}$ and $\{l_1, l_2, ..., l_{p-q-1}\}$ are two ordered subsets of integers chosen so that

$$\{j_1, j_2, ..., j_q, j_{q+1}\} \cup \{k_1, k_2, ..., k_q\} = \{1, 2, ..., p\}.$$

Similarly, the set of species is partitioned into a subset of *q* species $B_{h_1}, B_{h_2}, ..., B_{h_q}\ (1 < h_1 < h_2 < ... < h_q < n)$ that *are eliminated*, or, *not involved* in the OR and a subset *of n-q* species $B_{i_1}, B_{i_2}, ..., B_{i_{n-q}}\ (1 < i_1 < i_2 < ... < i_{n-q} < n)$ that *are involved* in the OR. Again, here $\{h_1;h_2;...;h_q\}$ and $\{i_1;i_2;...;i_{p-q}\}$ are two ordered subsets of integers chosen so that $\{h_1, h_2, ..., j_h\} \cup \{i_1, i_2, ..., i_{n-q}\} = \{1, 2, ..., n\}$.

A direct RR depends on both the selection of the *q+1* elementary reactions $r_{i_1}, r_{i_2}, \ldots, r_{j_q}, r_{j_{q+1}}$ that *are involved* in a direct RR and the *n-q* species $B_{i_1}, B_{i_2}, \ldots, B_{i_{n-q}}$ that *are involved* in the OR. Hence, a direct RR may be denoted by $R(r_{j_1}, r_{j_2}, ..., r_{j_q}, r_{j_{q+1}}, B_{i_1}, B_{i_2}, ..., B_{i_{n-q}})$.

The general equation of a direct RR is consequently Eq.(17).

$$R(r_{j_1}, r_{j_2}, ..., r_{j_q}, r_{j_{q+1}}, B_{i_1}, B_{i_2}, ..., B_{i_{n-q}}) = \sum_{k=1}^{q+1} \sigma_{jk} r_{jk} \qquad (17)$$

Substituting Eq.(13) into Eq.(17) and requiring the species $B_{h_1}, B_{h_2}, \ldots, B_{h_q}$ to disappear results in the following set of homogeneous linear equations:

$$\begin{aligned}
&\nu_{j_1,h_1}\sigma_{j_1} + \nu_{j_2,h_1}\sigma_{j_2} + ... + \nu_{j_q,h_1}\sigma_{j_q} + \nu_{j_{q+1},h_1}\sigma_{j_{q+1}} = 0\\
&\nu_{j_1,h_2}\sigma_{j_1} + \nu_{j_2,h_2}\sigma_{j_2} + ... + \nu_{j_q,h_2}\sigma_{j_q} + \nu_{j_{q+1},h_2}\sigma_{j_{q+1}} = 0\\
&\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\\
&\nu_{j_1,h_q}\sigma_{j_1} + \nu_{j_2,h_q}\sigma_{j_2} + ... + \nu_{j_q,h_q}\sigma_{j_q} + \nu_{j_{q+1},h_q}\sigma_{j_{q+1}} = 0
\end{aligned}$$

The solution of this system of homogeneous linear equations [73] is:

$$\sigma_{j_k} = \begin{vmatrix}
\nu_{j_1,h_1} & \nu_{j_1,h_2} & \dots\dots\dots & \nu_{j_1,h_q} & 0\\
\nu_{j_2,h_1} & \nu_{j_2,h_2} & \dots\dots\dots & \nu_{j_2,h_q} & 0\\
\dots\dots & \dots\dots & \dots\dots & \dots\dots & \dots\\
\nu_{j_{k-1},h_1} & \nu_{j_{k-1},h_2} & \cdots & \nu_{j_{k-1},h_q} & 0\\
\nu_{j_k,h_1} & \nu_{j_k,h_2} & \dots\dots\dots & \nu_{j_k,h_q} & 1\\
\nu_{j_{k+1},h_1} & \nu_{j_{k+1},h_2} & \cdots & \nu_{j_{k+1},h_q} & 0\\
\dots\dots & \dots\dots & \dots\dots & \dots\dots & \dots\\
\nu_{j_q,h_1} & \nu_{j_q,h_2} & \dots\dots\dots & \nu_{j_q,h_q} & 0\\
\nu_{j_{q+1},h_1} & \nu_{j_{q+1},h_2} & \cdots & \nu_{j_{q+1},h_q} & 0
\end{vmatrix} \qquad (18)$$

Substituting Eq.(18) into Eq.(17) gives the following general formula for a direct RR:

$$R(r_{j_1}, r_{j_2}, ..., r_{j_q}, r_{j_{q+1}}, B_{i_1}, B_{i_2}, ..., B_{i_{n-q}}) =
\begin{vmatrix}
\nu_{j_1,h_1} & \nu_{j_1,h_2} & \dots\dots\dots & \nu_{j_1,h_q} & r_{j_1}\\
\nu_{j_2,h_1} & \nu_{j_2,h_2} & \dots\dots\dots & \nu_{j_2,h_q} & r_{j_2}\\
\dots\dots & \dots\dots & \dots\dots & \dots\dots & \dots\\
\nu_{j_q,h_1} & \nu_{j_q,h_2} & \dots\dots\dots & \nu_{j_q,h_q} & r_{j_q}\\
\nu_{j_{q+1},h_1} & \nu_{j_{q+1},h_2} & \cdots & \nu_{j_{q+1},h_q} & r_{j_{q+1}}
\end{vmatrix} \qquad (19)$$

The most remarkable property of the direct RRs is their uniqueness. In particular, direct RRs are independent of the way they are generated. This property may be used to develop a computationally more effective algorithm of enumeration of the direct RRs which is described next. It should be noted that this new general approach was suggested by the theory of response reactions (RERs).

The RR network for hydrogen gas-phase oxidation reaction [26] presented represents the application of the RR network approach to a relatively complex, single OR chemical reaction system. The topology of this network reveals an unusual feature. Namely, so far, it was thought that, for reaction mechanisms involving a finite number of elementary reactions, reaction networks should be also finite. The chemical reaction systems considered by Professor Fishtik in [41,49,50] possessed compact and finite RR networks. However, in some cases, the thermodynamic and kinetic constraints imposed on a RR network may be satisfied only by drawing an infinite network. It was concluded that for complex reaction mechanisms, an infinite RR network is rather a rule than an exception [26].

2.2 Reduction and Simplification of Complex Kinetic Mechanisms. Reaction Route Graphs – a New Theoretical Tool to Study Complex Kinetic Mechanisms

Traditionally, one of the most frequently addressed issues within the kinetic mechanisms is the topological description of complex chemical reaction networks. More recently, complex biochemical networks were discussed within a rather general mathematical network theory. A universal characteristic of the graph-theoretical approach used for the topological description of chemical reaction networks was that each node, or vertex, represented a single species, while the branches, or edges, represented the species connectivity consistent with the elementary reaction steps encompassing the mechanism.

Within this research, Professor Fishtik developed a new type of reaction networks referred to as reaction route (RR) graphs. The main idea behind the RR graph theory was to associate the branches directly with the elementary reactions while additionally requiring the nodes to satisfy the quasi-steady state (QSS) conditions for the intermediates and terminal species. More specifically, this approach may be succinctly formulated as follows. For a given mechanism, abovementioned four unique topological characteristics could be defined as follows:

a) direct full routes (FRs) - a RR that eliminates all intermediates while pertaining all of the terminal species thus producing an overall reaction (OR);

b) empty routes (ERs) - a RR that eliminates all species, both intermediates and terminal species, thus producing a reaction in which all of the stoichiometric coefficients of the species are equal to zero (called zero reaction);

c) intermediate nodes (INs) – nodes at which the rates of the elementary reactions satisfy the QSS for the intermediate species;

d) terminal nodes (TNs) - nodes at which the rates of the elementary reactions satisfy the QSS conditions for the terminal species.

These fundamental topological features of a mechanism were further converted into a RR graph by realizing that that each IN can be viewed as a central node in a RR sub-graph. Within this approach the realization and enumeration of RR graphs was reduced to the problem of balancing the peripheral nodes in the RR sub-graphs according to the list of FRs, ERs, INs and TNs.

A corresponding RR graph was further translated into an electrical circuit network by associating each elementary step with a characteristic resistance and considering the overall reaction as a power source. As a result, one can use the well-developed and powerful methods of electrical networks to rationalize, reduce, and simplify complex kinetic mechanisms.

Finally, it was anticipated that the algorithms accompanying the RR reaction network approach will be translated into a computer code thus resulting into a new powerful tool for studying complex kinetic mechanisms.

Based on the RERs formalism, Professor Fishtik developed a completely new approach for the generation and simplification of kinetic mechanisms for complex reaction systems. This research has several fundamental and practically important goals for the enumeration and simplification of the kinetics of complex multiple chemical reaction systems:

a) computer generation of a comprehensive and unique global chemistry, *i.e.*, the list of RERs, from the given list of species;

b) selection of the dominant overall reactions;

c) determination of the coupling among chemical reactions and how it may be avoided;

d) determination of the quasi-steady state species;

e) use of the quasi-steady state approximation to derive stoichiometrically unique and decoupled reduced kinetic mechanisms;

f) determination of the necessary conditions that allow the mechanism reduction;

g) generation and enumeration of a unique set of reaction routes for every RER comprising the reduced mechanism;

h) development of a software based on the proposed algorithm and its interfacing with existing programs such as Chemkin;

i) comparison of the computational results obtained with the simplified kinetics for complex flows against numerical simulations with the complete kinetic models as well as experimental data.

2.3. Microkinetic Modeling in Heterogeneous Catalysis

Microkinetic model consists of the set of elementary reactions along with their rate constants for a heterogeneous catalytic reaction. In complex heterogeneous catalytic reaction systems, the surface coverages of the intermediates may be written in terms of the affinities of the elementary reactions in strictly speaking, an infinite number of ways. As a consequence, De Donder relations may be partitioned into contributions associated with arbitrarily selected overall reactions. Apparently, there is no mathematical error in this arbitrariness because De Donder relations are (and must be!) independent of the partitioning. However, an arbitrary set of De Donder relations is neither an essential feature of a chemical system nor an explanation of anything.

As Professor Fishtik mentioned, the property of De Donder relations to be partitioned into contributions coming from IRs and ORs was a gateway to gain a deeper insight into many aspects of the microkinetics of heterogeneous catalytic reactions.

Within the research [16,38,39,52,54,58,61, 63-65,70,81,82], taking into account the problem of arbitrariness of De Donder relations from the viewpoint of the theory of RRs, the robust kinetic expressions based on detailed molecular mechanisms coupled with predicted energetics of the elementary steps were developed. The main idea was to combine the theory of reactions routes, with the rate equations of the heterogeneous catalytic processes formulated in terms of affinities and commonly known as De Donder relations. It was concluded that there existed a direct interrelationship between De Donder relations and the theory of RRs. To be able to envisage this interrelationship, it was still necessary to extend the theory of RRs, which were defined as a linear combination of the elementary reactions that eliminated all of the intermediates. This conventional type of RRs produces ORs that involve only a specified number of terminal species. For this research purposes, however, it was necessary to introduce a different type of RRs defined as a linear combination of a specified set of elementary reactions that eliminated all but one of the intermediates, thus producing a reaction that involved only one intermediate and a specified number of terminal species, *i.e.*, IRs. In fact, the IRs represent the "chemical solution" of the substitution problem. In other words, the IRs involve only one intermediate and, hence, are a simple means to express the surface concentrations of the intermediates through the affinities of intermediate reactions. From general considerations, it is clear that there exists a certain interrelationship among elementary reactions, IRs and ORs. Professor Fishtik *et al.* found this interrelationship to be expressed by very simple equations. Concomitantly, these equations offer an interesting interpretation of the linear interrelationship between the elementary, intermediate, and overall reactions. Namely, they may be treated as reduced RRs, showing how an elementary reaction may be linearly combined with IRs so as to eliminate the intermediates and arrive at an OR. Because the affinities are a function of state, similar equations hold for the affinities, thus opening the door to the desired interrelationship between the affinities of the elementary reactions and the affinities of the IRs and ORs. The direct consequence of the mechanistic formalism developed was that De Donder relations are naturally partitioned into contributions coming from IRs and ORs. Because for a given mechanism both the IRs and ORs are unique and their number is finite, so is the partition of De Donder relations. In other words, for any set of elementary reactions comprising the detailed chemistry of a heterogeneous catalytic process, the enumeration of IRs, ORs, and reduced RRs implies concomitantly the enumeration of a finite and unique set of De Donder relations.

For the general case of a heterogeneous catalytic chemical reaction system, the species participating in the ERs of the catalytic mechanism were divided into: (i) active sites on the surface of the catalyst S; (ii) intermediates (surface) species $I_1;I_2;...;I_q$; and (iii) terminal (gas phase reactants and products) species $T_1;T_2;...;T_n$. Thus, the mechanism was described by the following set (Eq.(20)) of p ERs denoted by s_j.

$$s_j = \alpha_{j0}S + \sum_{k=1}^{q} \alpha_{jk} I_k + \sum_{i=1}^{n} \beta_{ji} T_i = 0; \quad j = 1,2,.., p \qquad (20)$$

As usual, it was assumed that the stoichiometric coefficients α_{j0}, α_{js} and β_{ji} took on positive values for products and negative for reactants. The rank of the stoichiometric matrix is $m \leq p$ and, consequently, the ERs are not all linearly independent. Nonetheless, all kinetically distinct ERs must be considered. Each ER is characterized by its affinity A_j ($j = 1,2,...,p$) that is defined as usual Eq.(21).

$$-\frac{1}{RT} A_j = -\ln K_j + \alpha_{j0} \ln \theta_0 + \sum_{k=1}^{q} \alpha_{jk} \ln \theta_k + \sum_{i=1}^{n} \beta_{ji} \ln P_i; \quad j = 1,2,...,p \qquad (21)$$

Here $K_j = \vec{k}_j / \overleftarrow{k}_j$ is the equilibrium constant of the jth ER, $\vec{k}_j$ and $\overleftarrow{k}_j$ are rate constants of the jth forward and reverse reaction, θ_0 is the fraction of the free (uncovered) surface of the catalyst, θ_k is the fraction of the surface occupied by the intermediate I_k and, P_i is the partial pressure of the terminal species T_i. The species site coverages are subject to site balance, *i.e.*

$$\sum_{k=1}^{q} \theta_k + \theta_0 = 1 .$$

The ERs written in the form of Eq.(20) are suitable for a thermodynamic analysis. For kinetic considerations, however, it is useful to distinguish between reactants and products by writing them as

$$\vec{\alpha}_{j0} S + \sum_{k=1}^{q} \vec{\alpha}_{jk} I_k + \sum_{i=1}^{n} \vec{\beta}_{ji} T_i = \overleftarrow{\alpha}_{j0} S + \sum_{k=1}^{q} \overleftarrow{\alpha}_{jk} I_k + \sum_{i=1}^{n} \overleftarrow{\beta}_{ji} T_i$$

where the arrows → and ← designate reactants and products, respectively. With this notation, all of the stoichiometric coefficients have positive values. Then, the rates or turn-over frequencies (TOFs) of the ERs are given by

$$r_j = \vec{r}_j - \overleftarrow{r}_j = \vec{r}_j \left[1 - \exp\left(-\frac{A_j}{RT} \right) \right]$$

where

$$\vec{r}_j = \vec{k}_j \theta_k^{\vec{\alpha}_{j0}} \prod_{k=1}^{q} \theta_k^{\vec{\alpha}_{jk}} \prod_{i=1}^{n} P_i^{\vec{\beta}_{ji}} = \vec{A}_j e^{\frac{\vec{E}_j}{RT}} \theta_k^{\vec{\alpha}_{j0}} \prod_{k=1}^{q} \theta_k^{\vec{\alpha}_{jk}} \prod_{i=1}^{n} P_i^{\vec{\beta}_{ji}} \qquad (22)$$

Here $\vec{A}_j$ and $\vec{E}_j$ are the pre-exponential factors and activation energies of the ERs in the forward direction. A linear combination of the ERs $s_1;s_2;...;s_p$ that eliminates a specified number of either intermediate or terminal species is called a reaction route (RR). A RR may, therefore, be expressed as

$$RR = \sum_{j=1}^{p} \sigma_j s_j \qquad (23)$$

where, $\sigma_1, \sigma_2,..., \sigma_p$ are the so-called stoichiometric numbers. Each RR produces an overall reaction (OR) denoted by R that may be obtained by substituting the ERs, Eq.(20), into Eq.(23).

Authors [61] employed a systematic method of analysis and reduction of a microkinetic mechanism that was based on the theory of RRs. The first step in this analysis was the enumeration of a unique set of RRs that showed how the given set of ERs comprising the mechanism could be linearly combined so as to eliminate all of the surface intermediates and to arrive at the overall reaction. Next, evaluating the contributions coming from individual RRs, the dominant RRs were determined. The ERs that did not appear in the dominant RRs were next omitted from the initial detailed mechanism thus resulting in a reduced mechanism. A further reduction of the mechanism was achieved employing the De Donder analysis.

Professor Fishtik addressed and solved several fundamental and practically important questions regarding the kinetics of heterogeneous catalytic reactions:

- What is the interrelationship between a detailed microkinetic model and the overall chemistry of a heterogeneous catalytic process?
- How to define and enumerate a unique set of reaction pathways that produce the overall chemistry?
- What is the interrelationship between the reaction pathways and the rate equations?
- How to discriminate and determine the dominant reaction pathways?
- How to derive a set of simplified rate equations?

This research was meant to result in a fundamentally new algorithm of generation, enumeration and discrimination of mechanisms for heterogeneous catalytic reactions. The computer software, planned to be developed based on this algorithm should find a broad range of applications in the very important area of modeling the kinetics of heterogeneous catalytic processes as well as the practically important problem of catalyst screening and design. This approach was successfully applied to model the kinetics of WGS (water-gas shift) reaction and steam reforming of methane.

3. Reaction Route Graphs in Chemical Kinetics

Directness of RRs and ORs, analyzed above, was already proven to be fruitful in kinetic modeling of multiple chemical reaction systems. When combined with reliable discrimination criteria among RRs and ORs such an analysis could be of enormous practical usefulness in understanding and predicting reaction kinetics and selectivity. For complex, in a multiple chemical reaction system including a large number of intermediates and elementary steps, the number of direct RRs and ORs, although finite and unique, may be extremely large. Obviously, in such cases the generation of direct RRs by hand, as well as discrimination among them, could be overwhelming. It would be consequently, important to implement the developed algorithms in a computer code.

A theory and algorithm for reaction route network analysis was developed in analogy with electrical networks and was based on the combined use of reaction route theory, graph theory, and Kirchhoff's laws [6,10,11,13,16,25,27,30,41,43,51,66,69,71,75,76, 81,83-85]. The result is a powerful new approach of "reaction route" graphs that is useful in not only topographical representation of complex reactions and mechanisms but, when combined with techniques of electrical network analysis, is able to provide revealing insights into the mechanism as well as the kinetics of the overall reactions involving multiple elementary reaction steps including the effect of topological constraints. Unlike existing graph theory approaches of reaction networks, the approach developed by Professor Fishtik is suitable not just for linear, but for non-linear kinetic mechanisms as well and for single and multiple overall reactions. The theoretical approach for the case of a single overall reaction involving minimal kinetic mechanisms (unit stoichiometric numbers) was developed. The utility of the new reaction route graph theory was illustrated by applying the proposed algorithm to the analysis, simplification and reduction of the kinetics of enzyme and surface catalyzed single overall reaction mechanisms.

4. Accurate Thermochemistry from Group Additivity and Methods *Ab Initio*

Accurate thermochemistry for molecular species is of crucial importance in chemical sciences and many technologies. An especially high demand in accurate thermochemistry is in the area of kinetic simulations of complex physicochemical systems, such as combustion, atmospheric processes, chemical vapor deposition, *etc.* Currently, two major groups of methods are used to evaluate the thermodynamic characteristics of molecules, namely, quantum chemical (density functional theory and *ab initio*) and empirical (group additivity (GA) and molecular mechanics) methods. The recent dramatic developments in computer technologies and, concomitantly, in quantum chemical methodologies resulted in tremendous progress in computational capabilities for the evaluation of accurate thermochemical data for large molecules. Now, high level *ab initio* calculations are done routinely. Surprisingly, despite these achievements, the importance of the classical GA methods is not diminishing. The GA methods were shown to be a valuable, effective and inexpensive technique for the estimation of thermodynamic properties of pure species even in the era of supercomputers. Moreover, the basic ideas of the GA methods are extensively used in converting the total energies (enthalpies) obtained from *ab initio* calculations into conventional thermodynamic functions.

Although the output of *ab initio* calculations, *i.e.*, the total energies of the species, are extremely accurate, the conversion of these quantities into conventional thermochemical data, *e.g.* enthalpy of formation of the species, continues to be the bottleneck in the final accuracy of *ab initio* methods. Firstly, the conversion requires the selection of a set of reference species for which the experimental thermochemical data are accurate. Secondly, the conversion requires the adoption of certain reaction schemes, such as formation, isodesmic, homodesmic reactions. Both of these requirements are difficult to meet. That is, accurate experimental thermochemical data for the reference species are often absent while the reaction schemes are selected arbitrarily.

The objective of the study was to develop and apply a fundamentally new methodology to extract accurate thermochemical data from both *ab initio* and GA methods [5,32,37,57,60]. The fundamental background of this new approach lied in the discovery according to which the procedure for converting the total energies from *ab initio* calculations into conventional thermochemical data is entirely equivalent to that employed in the GA methods. In order to visualize this analogy, there was employed the formalism of response reactions (RERs). More specifically, Professor Fishtik proved that the residuals in the ordinary least squares GA analysis may be partitioned into a sum of contributions associated with a new type of RERs referred to as

GA RERs. It was proved then that the special types of reactions employed in the *ab initio* methods were just a particular case of the GA RERs thus providing a direct link to GA methods. Using the RERs formalism not only resulted in a substantial improvement of the accuracy of the thermochemical data obtained from *ab initio* and GA methods but also provided a deeper insight into the complex relation between the structure of the species and their thermodynamic characteristics.

Briefly, this approach could be formulated as follows. Firstly, it was shown that the main assumption of the GA methods according to which chemical species could be "constructed' from a specified number and type of structural units, or groups could be formally appended to the conventional response reactions (RERs) formalism previously deduced from chemical thermodynamics and kinetics. As a result, one can define and generate a stoichiometrically unique class of GA RERs that have a remarkable property. Namely, the calculated property changes of the GA RERs are equal to zero. For instance, if the property of the species is the enthalpy of formation, then a GA RER should be thermo-neutral, *i.e.*, have an enthalpy change equal to zero. Secondly, the traditional ordinary least squares (OLS) GA analysis is modified so that the analogy between GA methods, stoichiometry, chemical thermodynamics and kinetics becomes transparent. Using this analogy, a hitherto unnoticed identity for the overall statistical outputs of the GA methods was derived. Thus, it was proved that the residuals of the OLS statistical analysis could be uniquely partitioned into a sum of contributions associated with GA RERs. This finding provided a new interpretation of the GA methods as well as a powerful tool for enhancing their accuracy. In particular, the GA calculations can be performed without evaluating the group values! Finally, it was proved that the procedure of converting the total enthalpies obtained from *ab initio* methods into conventional thermochemical data follows precisely the same lines as the GA methods.

The developed approach has several fundamental and practically important goals in both theoretical thermochemistry and physical chemistry:

1. Computer generation of a comprehensive and unique set of reactions preserving the detailed structure and thermodynamic functions of a given set of molecules.
2. Accurate evaluation of thermochemical data from GA and *ab initio* methods.
3. Direct comparison between the performance of GA and *ab initio* methods.
4. Determination of the species for which the classical and electronic structure is poorly correlated with the thermochemical data (outliers in the statistical analysis).

One of the most appreciated consequences of the developed optimization approach, however, is its remarkable unique stoichiometric representation. This representation demonstrates that the output of any computational thermochemistry analysis is uniquely determined by a list of reference species and their group matrix. Once these two stoichiometric characteristics are specified, a unique solution of the main computational thermochemistry problem is accessible in two different nevertheless equivalent forms.

Research along these lines was intended to result in a computer code that that would automatically generate accurate thermochemical data from *ab initio* and GA methods and would find broad applications in the very important area of theoretical thermochemistry. In particular, it was anticipated to interface the computer code with existing programs such as Gaussian and Chemkin.

Short biography of Professor Ilie Fishtik

Ilie Fiştic (English pronunciation, *Fishtik*) was born on August 9, 1953 in the Sofia village of the Drochia district (Republic of Moldova), in the family of Tudor and Agafia Fiştic. He graduated from the high school in 1970. During the 1970–1975 years he studied at the Faculty of Chemistry of the State University of Chisinau. In the 1973 year he married Maria Hristea, a student at the same faculty. In 1980, Ilie Fishtik defended his PhD in chemistry at the Moscow Institute of Electrochemistry of the USSR Academy of Sciences, Russian Federation, in the area of electrochemistry.

After graduating from the university, during the 1975–1996 years, Ilie Fiştic worked at the laboratory of Physicochemical Methods of Research and Analyses of the Institute of Chemistry, as a junior scientific researcher, then a senior and principal scientific researcher. During this time, with a frequent co-author Dr. Ion Vatamanu (in the scientific literature signed as *I.I. Vataman*), original approaches and methodologies in the field of electrochemistry and analytical chemistry were developed. In the period 1983–1996, together with Professor Igor Povar, his disciple, new concepts of non-classical, formal chemical thermodynamics were introduced and developed.

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Between 1992 and 1996 Professor Fishtik accomplished joint research with the well-known Hungarian Scientist István Nagypál, where the sensitivity analysis of multiple chemical equilibria was developed and unnoticed identities in chemical thermodynamics were derived. In 1996 the notion of response reactions, an interpretive concept in chemical thermodynamics, was introduced for the first time.

Since 1999 Dr. Fishtik worked as a university Professor at the Department of Chemical Engineering of the Polytechnic Institute of Worcester, U.S.A.

He published over a hundred papers of great fundamental and applied scientific value in the most prestigious journals in the world: *Journal of Physical Chemistry A* and *B, Journal of American Chemical Society*, *Pure and Applied Chemistry*, *Journal of the Chemical Society*, *Faraday Transactions*, *Chemical Engineering Communications*, *Chemical Engineering Science*, *Physical Chemistry*, *Zeitschrift für Naturforschung*, *Journal of Chemical Physics*, *Journal of Mathematical Chemistry*, *Journal of Electroanalytical Chemistry* and many more.

Professor Fishtik' main research areas of interest at the Department of Chemical Engineering of the Polytechnic Institute of Worcester were chemical thermodynamics, kinetics and heterogeneous catalysis. A large body of research Professor Fishtik performed jointly with Professor Ravindra Datta within the above mentioned Department. They applied the concept of stoichiometric uniqueness of several chemical reaction systems, deduced in the field of chemical thermodynamics, kinetics and catalysis. Professor I. Fishtik taught a number of disciplines: Introduction to Chemical Engineering, Chemical Reaction Engineering, Unit Operations and Thermodynamics, Advanced Thermodynamics, Special Topics in Chemical Kinetics, Heterogeneous Catalysis.

Professor Fishtik was awarded by the Academy of Sciences of Moldova (1990), the UK Royal Society of Chemistry Award for International Authors (1998) and the US National Research Council, Research Associateship Award (2004). His publications have been cited in over a thousand of scientific papers.

Conclusions

Brief biographical data as well as the main scientific achievements of the Professor Ilie Fishtik in the fields of chemical thermodynamics, kinetics and heterogeneous catalysis are succinctly presented and analyzed. The references of this paper contain the scientific publications of Professor Fishtik except for the papers published in the conference collections during the years 1975-1996, in the chronological order, starting with the most recent ones.

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Short biography of the author

Professor Dr. Igor Povar is the head of the laboratory "Physicochemical Methods of Research and Analysis" of the Institute of Chemistry in Chisinau (Republic of Moldova).

Graduated in 1983 from the Faculty of Chemistry of the Moldova State University and began working at the Institute of Chemistry of the Academy of Sciences of Moldova, in the group of Professor Fishtik. Defended his doctoral thesis in chemistry (specialty Physical Chemistry) at the Institute of Solid State Chemistry of the Russian Academy of Sciences, Ekaterinburg, under the leadership of Professor Fishtik Ilie and Dr. Vatamanu Ion.

Together with Professor Fishtik, new concepts and theory of non-classical, formal chemical thermodynamics were introduced and developed: thermodynamics of complex chemical equilibria in the heterogeneous system "solid phase – saturated aqueous solution, thermodynamic basis for apparent solubility product, Pourbaix diagrams derivation in the presence of polynuclear species in solution, computation of the complexation degree in linear-approximation etc. [107,109,110,114,117,118,120-127, 129,132].

Obtained in 1998 the title of Doctor habilitate in chemistry. Carried out, during 2001-2009, scientific research at the University of Western Ontario in London, Canada. Author and co-author of 4 monographs and textbooks, over 300 scientific publications. Fields of scientific interest: physical chemistry, especially chemical thermodynamics and its application in ecological chemistry, analytical chemistry and chemistry of complex compounds.

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