THERMODYNAMIC FRAMEWORK FOR DESIGN OF REACTION RATE EQUATIONS AND SCHEMES

Miloslav PEKAŘ

Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic; e-mail: pekar@fch.vutbr.cz

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It has been shown previously that rational thermodynamics provides general foundations of mass-action kinetic law from the principles of continuum, irreversible thermodynamics. Practical outcomes of this phenomenological theory are analyzed and compared with traditional kinetic approaches on the example of N_2O decomposition. It is revealed that classical rate equations are only simplified forms of a polynomial approximation to a general rate function proved by the continuum thermodynamics. It is also shown that various special considerations that have been introduced formerly as additional hypothesis to satisfactorily describe experimental data are naturally included in the thermodynamic approach. The method, in addition, makes it possible to obtain more general mass-action-type rate equations that give better description of experimental data than the traditional ones. The method even reverses the classical kinetic paradigm – reaction scheme directly follows from the rate equation. Data fitting by this method also indicates connections to distinctions between processes at the molecular level and their representation by some macroscopic reaction network. The role of dependent and independent reactions in reaction kinetics and reaction schemes is clarified. A selected example demonstrates that this thermodynamic methodology may improve our design and understanding of thermodynamically and mathematically necessary and sufficient reaction schemes. The phenomenological theory thus sheds new, "thermodynamic" light on what has been and is done by generations of kineticists and gives new hints how to do it in a way consistent with non-equilibrium thermodynamics.

Keywords: Kinetics; Reaction mechanisms; Rate equations; Reaction networks; Thermodynamics.

1. INTRODUCTION

Chemical and chemical engineering kinetics has developed into an established discipline indispensable especially in applied research or industrial chemistry. One of its most important outputs is the design of reaction rate equations and reaction mechanisms or networks which are called hereinafter reaction schemes. Reaction schemes and rate equations are usually very

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closely related. Laboratory experiments reveal products that are formed from an initial reacting mixture as well as intermediate species formed during the transformation of reactants into the products, detect concentration changes of perhaps all constituents of reacting mixture during the reaction time and also the temperature effects. Based on this information a potential reaction scheme is proposed that includes all detected constituents. To each step of the scheme a rate equation, mostly of the mass-action type, is attributed. The resulting rate equations are fitted to experimental data to determine their parameters (rate constants) and then used, e.g., for reactor design. When more potential mechanisms or networks are proposed, experimental data fitting is used to select the most probable one. As a rule, the label "reaction mechanism" is appropriated to a set of real elementary reactions whereas a system of reaction steps which need not necessarily represent individual molecular events is called a "reaction network". The method that is discussed here should apply to both mechanisms and networks; therefore, no special distinction is made and only the name "scheme" is used.

There is no definite and full theory for predicting reaction schemes and what is now known about mechanisms or networks consists largely of empirical classification[1]. Kinetic experience has collected a number of clues and rules for designing schemes[1]. Recently, Ross published an overview of some new approaches to deducing reaction schemes based on controlled (perturbation) experiments[2]. More and more often methods of molecular modeling, in particular the quantum chemistry calculations, are used to support the finding of reaction mechanisms by looking for the most probable intermediates and their location on the reaction coordinate.

The traditional kinetic mass-action law, i.e., formulating reaction rate as a difference of two terms representing forward and reverse reaction rates each being in the form of product of rate constants and respective concentrations, plays a central role in the design of rate equations corresponding to the selected scheme. Phenomenologically, the kinetic mass-action law is an empirical law and its theoretical motivations or even proofs originate in molecular (statistical) theories. Perhaps the only phenomenological proof was given by Samohýl within the framework of rational thermodynamics[3–6]. Before going into details, attempts to relate (phenomenological, macroscopic) chemical reaction kinetics and thermodynamics will be briefly reviewed. Sometimes, the derived rate equations are subjected to testing their thermodynamic consistency. This mostly means putting some restrictions for thermodynamic equilibrium (usually the minimum of the reaction Gibbs energy) in which the reaction rate should vanish (for review, see ref.[7]). During last decades the relationship of thermodynamics to chemical

kinetics has developed and progressed a substantial step further from the textbook attitudes that, with respect to a chemical reaction, thermodynamics says *if* and kinetics *how*.

Double, i.e., thermodynamic and kinetic, description of equilibrium initiated various thermodynamic consistency tests and modifications of rate equations written as the traditional kinetic mass-action law[8–15]. Some studies moved deeper into the relationship between kinetics and thermodynamics, particularly in respect to deriving the kinetic mass-action law from thermodynamic considerations or, at least, to prove its consistency with modern, non-equilibrium thermodynamic theories. Most of these works were made within the framework of extended irreversible thermodynamics. García-Colín and de la Selva[16] derived a "general phenomenological relation" which expresses the reaction rate as a function of powers of affinity. In paper by García-Colín et al.[17] it is claimed that the kinetic mass-action law was derived from the extended irreversible thermodynamics approach. In fact, this means some equation for the time derivative of reaction rate, which is dependent on affinity, heat and diffusion fluxes and some undetermined function. Resulting equation is of theoretical value but would not probably serve to practical chemical kinetics[7]. Fort et al.[18] published extended irreversible thermodynamic phenomenological model of non-equilibrium chemically reacting systems. The most important finding is that non-equilibrium correction to the specific entropy is an expression of the second power in the reaction rate. No explicit kinetic equation was found.

Lengyel in a series of papers[19–22] tried to generalize the kinetic Guldberg–Waage (mass-action) law using non-equilibrium thermodynamics based on Gyarmati's variational approach. Actually, he introduced this law into the non-equilibrium framework to rederive it again after some mathematical manipulations[7]. Its general form is really too general to be applicable in practical kinetics, particularly because it contains affinities in the forward and reverse reaction directions separately with no hint how to find them in reality. Similar conclusions can be made on the papers by Oláh[23–28].

Several studies on chemically reacting systems have come also from the continuum, especially rational thermodynamics[29–36]. Concerning chemical kinetics they usually led only to very general statements on the function form of the reaction rate, e.g., the reaction rate is a function of densities (i.e., mass concentrations) of components present in the reacting mixture, temperature, and gradients of density, temperature and deformations. No particular form of the function is derived. As noted above, perhaps the only exception is Samohýl's approach[3-6]. In fact, he was able to derive the mass-action kinetic law simply from thermodynamics. Samohýl really proved

that the reaction rate is a function of temperature and concentration but only in the reacting mixture of fluids with linear transport properties. Briefly, this is a mixture with (general) Newtonian flow behavior and, of course, with heat transfer and mass transport, i.e., a material model of broad interest for practical chemistry. In more complex material models the reaction rate can be a function of more variables than just temperature and concentration[29–36]. Thus, not only the mass-action law was proved but also its limited validity was clearly stated. Samohýl's thermodynamically consistent method has interesting consequences also for the design of reaction schemes that have been illustrated in our previous work[37]. The reaction scheme results directly from the rate equation.

The method and its potential have not been further investigated and tested, perhaps because the originals mostly gave the general mathematical basis only. It provides a well-defined thermodynamic framework for the design of reaction rate equations and schemes but there are no practical experience and comparisons with traditional approaches. It is the aim of this paper to further study this method and its application on a simple reaction example, to compare the obtained rate equations and schemes with those arrived at by the traditional approach and further, to exemplify the method, to explain its functioning and to enlighten both its power and limitations.

The decomposition of nitrous oxide was selected as the reaction to illustrate the rational thermodynamic method. This reaction has been studied for many years and a vast amount of experimental experience has been gathered. It should be stressed that it is not the aim of this paper to discuss or evaluate published data or reaction schemes for N_2O decomposition. The reaction should serve just as an illustrative example for equations resulting from the thermodynamic method, an example of what can be and cannot be obtained and expected from the thermodynamic methodology, and as a comparative test for traditional mass-action rate equations.

We are primarily interested in homogeneous reaction, i.e., in thermal or perhaps photochemical N_2O decomposition. The most simple and straightforward approach to description of kinetics of N_2O decomposition was through the time change (derivative) of its concentration (partial pressure). This approach was not universal over the whole range of N_2O initial pressures and it is commonly accepted that the reaction order changes from two to one and also the low and high pressure limits for the corresponding rate constant are reported[38]. Experimental studies were initiated by M. A. Hunter as early as 1905 [39]. In his experimental arrangement only bimolecularity could be stated. Bimolecularity was confirmed lately by

Hinshelwood and Burk[40] but the next contribution from the same laboratory[41] already reported on a combination of mono- and bimolecular processes. The complex nature of N_2O decomposition over the range of initial pressures was subsequently confirmed by E. Hunter[42], who also proposed three reaction steps (see below for details). It should be noted that these initial deductions were made mostly on the basis of the measured dependence of the reaction half-life on the initial pressure of N_2O.

With a rapid evolution of experimental techniques in the second half of the last century, more and more complex and sophisticated studies on N_2O decomposition appeared using, e.g., optical and photometric or mass spectroscopic methods, which resulted in revealing various possible intermediates or components in the reacting mixture. Many of them were reviewed in a comprehensive kinetics monograph[38] where the main reaction steps are given. Results are often given in terms of the formal first-order rate constant k (coefficient, more precisely), estimated from the equation $\mathrm{d}c_{\mathrm{N_2O}}/\mathrm{d}t = -kc_{\mathrm{N_2O}}$, which is pressure-dependent. From the later works let us cite only the detailed computer modeling study by Konnov and de Ruyck[43] where almost 30 potential reaction steps were collected from literature together with their activation energies and pre-exponential factors.

The paper is organized as follows: Section 2 briefly recapitulates the methodology and principles of its application in kinetic investigations. Sections 3–5 exemplify a variety of rate equations that can result from an experimentally determined composition of a reaction mixture on different levels of knowledge of intermediates and side-products, and show how the equations can be interpreted to devise a reaction scheme. Section 6 adds important notes on details of the procedure and explains how the reaction scheme appears in the rate equation. Section 7 stresses the most important general benefits of this methodology.

Examples demonstrate that the published schemes or rate equations are just special (simplified) results of the rational thermodynamic methodology, which offers also more general results. The methodology may even reverse the traditional paradigm in the rate-scheme research as is illustrated below.

2. THEORY AND ITS APPLICATION

For reader's convenience, the basic principles of the method are summarized in this section. More details can be found in original sources including the basics of continuum or rational thermodynamics[44]. Samohýl has proved[3–6], using all axioms of rational thermodynamics including the second law and indestructibility of atoms (no nuclear transformations

are considered), that in a reacting mixture of fluids with linear transport properties the reaction rate of an independent reaction is a function of temperature (T) and component densities only. As the densities are directly and simply related to the molar concentrations (c_i), this function can be reformulated as

$$\boldsymbol{J} = \boldsymbol{J}(T, c_1, c_2, \ldots, c_n) \qquad (2.1)$$

(n is the total amount of components in reacting mixture). Components of the vector $\boldsymbol{J}$ are the rates of all independent reactions (J_k), which are r in total, $\boldsymbol{J} = (J_1, J_2, \ldots, J_r)$. The number of independent reactions is found from the postulate of indestructibility of atoms expressed in terms of linear algebra[45]. Thus, all independent reactions generally have the same form of rate equation. It should be stressed that the otherwise trivial result (*2.1*) that is used by generations of kineticists and established by their experience was thus justified for the first time by a (phenomenological) theory and its limited validity for the linear fluids only was demonstrated.

General function (*2.1*) is then approximated by a polynomial of degree M in concentrations[3–6].

$$\boldsymbol{J} = \sum_{\beta=1}^{Z} \boldsymbol{k}_{\boldsymbol{\nu}_\beta} \prod_{\alpha=1}^{n} c_\alpha^{\nu_{\beta\alpha}}, \qquad \sum_{\alpha=1}^{n} \nu_{\beta\alpha} \leq M \qquad (2.2)$$

The vector $\boldsymbol{k}_{\boldsymbol{\nu}_\beta}$ contains polynomial coefficients. They are dependent on temperature only and can be interpreted as traditional rate constants[3–6,37]. Vectors $\boldsymbol{\nu}_\beta = (\nu_{\beta 1}, \nu_{\beta 2}, \ldots, \nu_{\beta n})$ contain the polynomial powers and are used also as subscripts to index various vectors of the polynomial coefficients ($\boldsymbol{k}_{\boldsymbol{\nu}_\beta}$). When used in subscripts of the vectors $\boldsymbol{k}_{\boldsymbol{\nu}_\beta}$ elements of the vectors $\boldsymbol{\nu}_\beta$ are written without commas and parenthesis. Note that the vector element $\nu_{\beta\alpha}$ determines the power at the concentration of component α in corresponding polynomial term. Total number of polynomial terms is given by

$$Z = \sum_{k=0}^{M} \frac{(n+k-1)!}{k!(n-1)!}. \qquad (2.3)$$

Equilibrium is defined as a state where the rates vanish, $\boldsymbol{J}^{\mathrm{eq}} = 0$. Consequently, the polynomial (*2.2*) with equilibrium concentrations should vanish as well. At the same time the relationships for equilibrium constants of all independent reactions should be valid.

$$K_p = \prod_{\alpha=1}^{n} (c_\alpha^{eq})^{P^{p\alpha}}, \quad p = 1, 2, ..., r \tag{2.4}$$

Here, K_p is the equilibrium constant of the p-th independent reaction and $P^{p\alpha}$ is the element of stoichiometric matrix, i.e., the stoichiometric coefficient of component α in reaction p. Note that at this moment only ideal systems are considered but including non-ideality through activities is straightforward[4,5], see also the last paragraph of this section. Using relations (*2.4*) some equilibrium concentrations can be expressed through the others and substituted into the vanishing equilibrium polynomial. The number of different concentrations in the equilibrium polynomial is thus reduced and polynomial terms with equal powers of the same concentrations can be gathered. The simplified equilibrium polynomial should vanish in every equilibrium, i.e., for arbitrary selection of the equilibrium concentrations. To satisfy this requirement some coefficients in the modified polynomial should be zero. This leads either to vanishing of some polynomial coefficients in the vector $\boldsymbol{k}_{\nu_\beta}$ or to a possibility of expressing some of its elements through the others and equilibrium constants[3–6]. Since the polynomial coefficients were proved to be functions of temperature only, these assertions are valid also off equilibrium. The final simplified rate equation then results. The method is inherently flexible – various versions of rate equations can be derived depending on the degree of approximating polynomial. All alternatives can be then subjected to confrontation with experimental reality. On the other hand, the form of the resulting rate equation (for a polynomial of given degree) does not depend on which reactions were selected as independent[4] as is also illustrated below. It should be stressed that the method does not consider the kinetic mass-action law *a priori* and does not construct any polynomials from rate equations of the mass-action type. The polynomial does not approximate mass-action equations but the general rate function described above. However, it will be shown below that the resulting rate equations can be interpreted within the mass-action tradition.

Let us point out that the approximation (*2.2*) is not just a polynomial approximation but a specific approximation subjected to thermodynamic conditions of reaction equilibria and what matters here is its kinetic consequences and not the approximation itself. Note also that the procedure of deriving the rate equations results in automatic fulfillment of the detailed balance, i.e., in principle, reversibility of all reaction steps and their equilibration when equilibrium of the reacting system is attained. Let us further

remark that the discussed procedure indicates that the detailed balance may be a consequence of the permanence of atoms[46].

To apply the method, components of a reacting mixture have to be determined first from experiments or perhaps also from quantum chemistry calculations. This is necessary for finding the number of independent reactions and stoichiometric matrix. Regarding our example of the N_2O reaction, first studies considered just the simplest stoichiometric equation, i.e., a mixture of nitrous oxide, molecular oxygen and nitrogen. With progress in experimental techniques more constituents were detected or assumed and the reacting mixture has started to be more complex. Therefore the thermodynamic methodology can be advantageously demonstrated on several reacting mixtures of increasing complexity and simulate application of the presented methodology by former investigators having had different level of experimental knowledge of the composition of reacting mixture.

Thermodynamic consistency of the method is rooted in the very proof of the function (*2.1*) during which all principal postulates of rational thermodynamics, not only the "second law", have been applied[3–6] and in the transformation of rate polynomial (*2.2*) using the equilibrium condition together with the temperature-only dependence of the polynomial coefficients, also proved by the rational thermodynamics. The resulting rate equation can be re-introduced into the entropy inequality (the "second law" of thermodynamics) which places another restriction on the values of the rate coefficients[4,5]. However, the restrictions can be analytically resolved only for very simple reacting systems (schemes). Realistic values of the rate coefficients should be thus obtained principally by the experimental data fitting, considering, as usual only those values that give non-negative concentrations.

The main steps of the method in the design of rate equation (and scheme) thus are[37]:

– to determine all relevant components of a reacting mixture, including intermediates;

– to construct polynomial (*2.2*) of a suitable degree (usually two or three), taking into account the selected set of independent reactions;

– to substitute some equilibrium concentrations from the expressions for the equilibrium constants of independent reactions, Eq. (*2.4*), in the equilibrium polynomial;

– to form the equilibrium polynomial in the remaining equilibrium concentrations;

– to apply the condition of universality of equilibrium to find which polynomial coefficients or their combinations are equal to zero[3–6,37], cf. section 6;

– to introduce the zero coefficients (combinations) into the original, non-equilibrium polynomial; the final rate equation results.

The rate equation is then applied to experimental data and the whole procedure can be repeated, e.g., with a polynomial of different degree, to obtain the best and realistic data description.

It should be noted that the described method does not *a priori* distinguish ideal and non-ideal systems. Examples given here are formulated in concentrations as in all original papers on N_2O decomposition and as it is the most frequent case in kinetics. The simplest way to take into account non-ideal systems is to transform the initial general rate function from the concentration- and temperature-dependent one an activity- and temperature-dependent form, which is quite an easy task[3–5], and express equilibrium constants in activities. All examples presented here would remain valid but concentrations should be replaced with activities.

3. REACTION MIXTURE CONTAINING N_2O, N_2, O_2

This simplest mixture was considered at the early beginning of investigations on N_2O decomposition; nowadays it is a history. Here it serves as an introductory illustration of the method. The mixture is composed of three components (n = 3); hence, only one independent reaction is possible. It can be best selected as the overall stoichiometric reaction

$$2\ N_2O = 2\ N_2 + O_2\ . \qquad (3.1)$$

Let us number the components as follows: 1 = N_2O, 2 = O_2, 3 = N_2.

The approximating first- and second-degree polynomials are identically zero. The third-degree polynomial gives the following equation

$$J = k_{200}(c_1^2 - K^{-1}c_2c_3^2), \qquad (3.2)$$

i.e., an ordinary mass-action law. Thus, the traditional rate equation is recovered and it is, in fact, the third-degree polynomial approximation to the general rate function (*2.1*). A non-traditional, more general equation can be obtained with the fourth-degree polynomial, which results in

$$J = k_{200}(c_1^2 - K^{-1}c_2c_3^2) + k_{300}(c_1^3 - K^{-1}c_1c_2c_3^2) +$$

$$+ k_{210}(c_1^2 c_2 - K^{-1} c_2^2 c_3^2) + k_{201}(c_1^2 c_3 - K^{-1} c_2 c_3^3) . \qquad (3.3)$$

In previous works[3–6,37] it was proposed to interpret rate equations obtained with the polynomial approximation as containing mass-action terms corresponding to the individual steps of reaction scheme. Equation (*3.3*) contains four such terms and the scheme corresponding to them is

$$\begin{aligned} &1.\quad 2\ N_2O = O_2 + 2\ N_2 \\ &2.\quad 3\ N_2O = N_2O + O_2 + 2\ N_2 \\ &3.\quad 2\ N_2O + O_2 = 2\ O_2 + 2\ N_2 \\ &4.\quad 2\ N_2O + N_2 = O_2 + 3\ N_2 . \end{aligned} \qquad (3.4)$$

It should be stressed that although only one independent reaction exists, four reactions appear to be significant in the rate equation (*3.3*). Scheme (*3.4*) just illustrates an additional interesting feature of the presented method – direct design of reaction schemes from kinetic equations.

Equation (*3.3*) can be further modified

$$\begin{aligned} J &= k_{200}(c_1^2 - K^{-1} c_2 c_3^2) + k_{300} c_1 (c_1^2 - K^{-1} c_2 c_3^2) + \\ &+ k_{210} c_2 (c_1^2 - K^{-1} c_2 c_3^2) + k_{201} c_3 (c_1^2 - K^{-1} c_2 c_3^2) = \\ &= (k_{200} + k_{300} c_1 + k_{210} c_2 + k_{201} c_3)(c_1^2 - K^{-1} c_2 c_3^2) \equiv \\ &\equiv k(c_1^2 - K^{-1} c_2 c_3^2) \end{aligned} \qquad (3.5)$$

where k is the concentration-dependent rate "constant" (coefficient, more precisely). Equation (*3.5*) expresses the reaction rate just with the mass-action term corresponding to the selected (and the only independent) reaction (*3.1*) only, but now the rate coefficient (k) is concentration-dependent.

Equation (*3.5*) allows to derive directly various historical proposals made *ad hoc* on the basis of experimental results that were inconsistent with the traditional simple mono- or bimolecular processes. Introducing the material balance for a batch system (Table I) we get

$$J = k[(a - x)^2 - K^{-1} x^3 / 2],$$

$$k = k_{200} + k_{300} a + (k_{210}/2 + k_{201} - k_{300}) x \equiv k_{200} + k_{300} a + \bar{k} x \qquad (3.6)$$

where $\bar{k}$ is concentration-independent. Experimental results suggest that $K >> 1$, i.e., reaction (*3.1*) is virtually irreversible. Then $J = k(a - x)^2$. As $dc_{N_2O}/dt = J^{N_2O} = -2J$, where J^{N_2O} is the rate of N_2O formation, we obtain the following differential equation for the batch system.

$$-dx/dt = -2(k_{200} + k_{300}a + \bar{k}x)(a - x)^2 \qquad (3.7)$$

Equation (*3.7*) can be formally rewritten as

$$-dx/dt = k_1(a + x) + k_2(a - x)^2 \qquad (3.8)$$

where $k_1 = 2(k_{200} + k_{300}a)(a - x)$ and $k_2 = 2\bar{k}x$. Equation (*3.8*) expresses the rate as a sum of monomolecular and bimolecular processes just as assumed by Musgrave and Hinshelwood[41], in our case with rate coefficients (k_1 and k_2) generally dependent on concentration.

Integrating Eq. (*3.7*) within the limits $\langle 0;t\rangle$ and $\langle 0;x\rangle$ we obtain

$$2t = (A/\bar{k})\ln|k_a + \bar{k}x| - B\ln|a - x| + C/(a - x) - (A/\bar{k})\ln|k_a| + B\ln|a| - C/a \qquad (3.9)$$

where

$$A = \bar{k}^2/(\bar{k}a + k_a)^2; \quad B = \bar{k}/(\bar{k}a + k_a)^2; \quad C = 1/(\bar{k}a + k_a)^2; \quad k_a = k_{200} + k_{300}a.$$

The examined reaction mixture was considered mostly in the first studies[39–42] which usually discussed the dependence of the reaction half-life ($t_{1/2}$) on the initial concentration (pressure) of nitrous oxide. It did not correspond either to the pure mono- or bimolecular process. From Eq. (*3.9*), this dependence is

TABLE I
Material balance for reaction mixture N_2O–N_2–O_2 in batch system

Time	Concentration		
	N_2O	O_2	N_2
0	a	0	0
t	$a - x$	$x/2$	x

$$t_{1/2} = \frac{\bar{k}(\ln|k_{200} + k_{300}a + \bar{k}a/2| - \ln|k_{200} + k_{300}a|) + \bar{k}\ln 2 + a(\bar{k}a + k_{200} + k_{300}a)}{2(\bar{k}a + k_{200} + k_{300}a)^2} . \quad (3.10)$$

Equation (*3.10*) has a finite limit as can be easily found using the l'Hospital rule

$$\lim_{a\to\infty} t_{1/2} = 1/2(\bar{k} + k_{300}). \quad (3.11)$$

This is in contrast to the first- or second-order rate equation and agrees with experimental findings on the high pressure limit.

Thermodynamic procedure thus can lead even within this simple reacting mixture directly to several conclusions that could not be derived using single traditional first- or second-order rate equation for the same reaction (*3.1*) and should be introduced as extra hypotheses. However, Eq. (*3.10*) is not flexible enough to fit all experimental data given, e.g., by Hunter[42]. Examples are given in Fig. 1; note that the trimolecular step (*3.4.2*) could be neglected.

Although the discussed approach gives better fit of experimental data than a simple traditional combination of the first- and second-order reac-

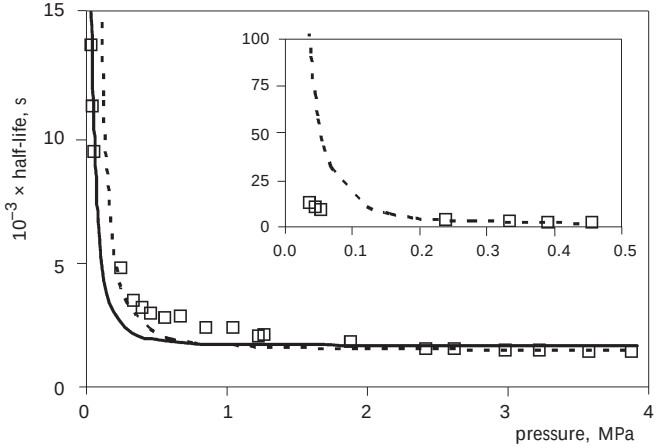

FIG. 1

Dependence of the reaction half-life on the initial pressure of nitrous oxide. Data points given by Hunter[42], lines calculated from Eq. (*3.10*) with $\bar{k}$, k_{200}, k_{300} equal to 0.018, 0.015, 0 (——) and 0.02, 10^{-6}, 0 (- - - -), respectively (inset is a detailed view at low initial pressures)

tion steps and offers an alternative to *ad hoc* models in the form of sum of rational functions[42], it cannot be considered as fully satisfactory. Thus, an attempt to describe the reaction of N_2O decomposition using a mixture of N_2O, N_2 and O_2 is to be considered unsuccessful. Already Hunter[42] proposed an explanation including also atomic oxygen, although its concentration could not be detected at that time.

4. REACTION MIXTURE CONTAINING N_2O, N_2, O_2, O

This is the most natural extension of the preceding reacting mixture and corresponds to those papers where also atomic oxygen was measured or, at least, considered in addition to the principal reactant and products. In this case $n = 4$ and two independent reactions are possible. Let us select them as perhaps the most logic and reasonable from the chemical standpoint.

$$\begin{aligned} &1.\quad N_2O = N_2 + O \\ &2.\quad O + N_2O = N_2 + O_2 \end{aligned} \qquad (4.1)$$

The first-degree approximating polynomial is identically zero. The second-degree polynomial gives the following rate equation.

$$\boldsymbol{J} = \boldsymbol{k}_{0010}(c_3 - K_1^{-1}c_2c_4) + \boldsymbol{k}_{0110}(c_2c_3 - K_2^{-1}c_1c_4) + \boldsymbol{k}_{0200}(c_2^2 - K_1K_2^{-1}c_1) \qquad (4.2)$$

The components are numbered as follows: 1 = O_2, 2 = O, 3 = N_2O, 4 = N_2; K_i is the equilibrium constant of reaction (*4.1.i*). Note that all vectors are two-component: $\boldsymbol{J} = (J_1, J_2)$, $\boldsymbol{k}_{ijlm} = (k'^{1}_{ijlm}, k'^{2}_{ijlm})$, J_i is the rate of reaction (*4.1.i*). To distinguish a vector component index from a simple power in superscripts the former is preceded by a comma. In this case, the traditional mass-action law corresponding to reactions (*4.1*) is not recovered and cannot even be considered as a second-degree polynomial approximation to the general function (*2.1*). Similarly as in the preceding part, Eq. (*4.2*) can be interpreted as describing the rate of the nitrous oxide decomposition by the following scheme.

$$\begin{aligned} &1.\quad N_2O = N_2 + O \\ &2.\quad O + N_2O = N_2 + O_2 \\ &3.\quad O + O = O_2 \end{aligned} \qquad (4.3)$$

It is interesting that this is just the scheme proposed by Hunter[42]. Besides the two independent reactions one additional step appears – a very logical and plausible recombination of atomic oxygen (*4.3.3*). Thus the rational thermodynamic approach directly proposes an experimentally acceptable scheme regardless of selected (a lower number) independent reactions; the scheme can even contain (thermodynamically) dependent steps. The dependence of reactions means here that the third step in (*4.3*) can be expressed as a difference between the second and first step.

It has been also generally proved that the resulting ("polynomial") rate equation does not depend on the selection of independent reactions[4]. That is, selecting, e.g., the pair $2\ N_2O = 2\ N_2 + O_2$ and $N_2O = N_2 + O$ as the set of independent reactions also leads to the form (*4.2*) but now the equilibrium constants refer to the new selected independent reactions. Because the proposed reaction scheme directly follows from the rate equation this further means that also the scheme is independent of the selection of independent reactions.

As in the preceding part let us assume that the reverse reactions can be neglected. From the stoichiometric algebra, the formation rates for nitrous oxide and atomic oxygen are

$$J^{N_2O} = -J_1 - J_2 \qquad J^{O} = J_1 - J_2 . \tag{4.4}$$

For a batch reactor it results

$$\mathrm{d}c_{N_2O}/\mathrm{d}t \equiv J^{N_2O} = (-k'^{1}_{0010} - k'^{2}_{0010})(c_3 - K_1^{-1} c_2 c_4) +$$

$$+ (-k'^{1}_{0110} - k'^{2}_{0110})(c_2 c_3 - K_2^{-1} c_1 c_4) + (-k'^{1}_{0200} - k'^{2}_{0200})(c_2^2 - K_1 K_2^{-1} c_1) \tag{4.5}$$

$$\mathrm{d}c_{O}/\mathrm{d}t \equiv J^{O} = (k'^{1}_{0010} - k'^{2}_{0010})(c_3 - K_1^{-1} c_2 c_4) +$$

$$+ (k'^{1}_{0110} - k'^{2}_{0110})(c_2 c_3 - K_2^{-1} c_1 c_4) + (k'^{1}_{0200} - k'^{2}_{0200})(c_2^2 - K_1 K_2^{-1} c_1) . \tag{4.6}$$

It is possible to recover classical mass-action balances for the scheme (*4.3*) as a special case of Eqs (*4.5*) and (*4.6*). Let us make the following considerations, cf. (*4.3*), (*4.5*) and (*4.6*)

$$-(-k'^{1}_{0010} - k'^{2}_{0010}) = k'^{1}_{0010} - k'^{2}_{0010} \Rightarrow k'^{2}_{0010} = 0$$

$$-k'^{1}_{0110} - k'^{2}_{0110} = k'^{1}_{0110} - k'^{2}_{0110} \Rightarrow k'^{2}_{0110} = 0$$

$$-k'^{1}_{0200} - k'^{2}_{0200} = 0 \Rightarrow k'^{1}_{0200} - k'^{2}_{0200} = 2k'^{1}_{0200} \tag{4.7}$$

and assume further that

$$k'^{1}_{0010} > 0; \quad k'^{2}_{0110} > 0; \quad k'^{1}_{0200} < 0 . \tag{4.8}$$

Note that generally there is no demand on non-negativity of polynomial coefficients which are interpreted as the rate constants. In simple reaction systems the entropic inequality may set such requirement directly[4,5] but generally the coefficients may be also negative. Introducing a new notation

$$k_1 \equiv k'^{1}_{0010}; \quad k_2 \equiv k'^{2}_{0110}; \quad k_3 \equiv k'^{1}_{0200} \tag{4.9}$$

the following results are finally obtained

$$-\mathrm{d}c_{\mathrm{N_2}}/\mathrm{d}t \equiv \mathrm{d}c_{\mathrm{N_2O}}/\mathrm{d}t = \\ = -k_1(c_{\mathrm{N_2O}} - K_1^{-1} c_{\mathrm{O}} c_{\mathrm{N_2}}) - k_2(c_{\mathrm{O}} c_{\mathrm{N_2O}} - K_2^{-1} c_{\mathrm{O_2}} c_{\mathrm{N_2}}) \tag{4.10}$$

$$\mathrm{d}c_{\mathrm{O}}/\mathrm{d}t = k_1(c_{\mathrm{N_2O}} - K_1^{-1} c_{\mathrm{O}} c_{\mathrm{N_2}}) - \\ - k_2(c_{\mathrm{O}} c_{\mathrm{N_2O}} - K_2^{-1} c_{\mathrm{O_2}} c_{\mathrm{N_2}}) - 2k_3(c_{\mathrm{O}}^2 - K_1 K_2^{-1} c_{\mathrm{O_2}}) \tag{4.11}$$

and also

$$\mathrm{d}c_{\mathrm{O_2}}/\mathrm{d}t = k_2(c_{\mathrm{O}} c_{\mathrm{N_2O}} - K_2^{-1} c_{\mathrm{O_2}} c_{\mathrm{N_2}}) + k_3(c_{\mathrm{O}}^2 - K_1 K_2^{-1} c_{\mathrm{O_2}}) . \tag{4.12}$$

Equations (*4.10*)–(*4.12*) represent just the classical mass-action expressions corresponding to the scheme (*4.3*) and containing only positive rate constants. Derivation of Eqs (*4.10*)–(*4.12*) demonstrates further that the traditional mass-action law for this scheme is a special, simplified case of the second-order polynomial approximation to the general function (*2.1*).

What about if some experiment shows that all three reactions (*4.3*) proceed and not just independent steps (*4.1*), if there such unambiguous experiment can exist at all? Algebra of stoichiometry tells[45] that just two reactions are sufficient to describe transformations of the detected constituents in the given reacting mixture. There is no need to use the rate of reaction (*4.3.3*), say J_3, besides the rates of reactions (*4.1*). However, the mass-action term corresponding to this dependent reaction appears in the rate equations derived for the two selected independent reactions, consequently, also this dependent reaction may affect reaction kinetics. The presented methodology clearly shows that equations for rates of independent reactions may contain “additional” (dependent) reaction terms.

Numerical simulations made with irreversible versions of the new equations (*4.5*), (*4.6*) and traditional equations (*4.10*), (*4.11*) clearly illustrate a much better potential of investigated methodology for description of experimental data. The curves calculated with the latter equations are still not sufficiently curved to fit Hunter's half-life data (see Fig. 2 for some of the best attainable fits). Data description is yet worse than with a simpler reaction mixture in the previous section. Traditional rate equations are not able to represent the large difference in half-lifes measured for low and high input pressures. On the other hand, the equations derived by the studied thermodynamic approach give quite a satisfactory fit shown in Fig. 3 and in Table II.

A substantial distinction between otherwise similar traditional and new equations consists in the rate coefficients. Whereas the traditional equations (*4.10*) and (*4.11*) contain the same coefficients (k_i) in corresponding terms in parentheses, analogous coefficients in the new equations (*4.5*) and (*4.6*) are not generally identical but are equal to different combinations (differences) of k'^{1}_{ijlm} and k'^{2}_{ijlm}. This distinction is rooted in Eq. (*4.4*) and also in the general form of polynomial rate equation (*4.2*). Although the formation rates of both N_2O and O contain the same parenthesis terms resembling mass-action concentration expressions (see Eqs (*4.5*) and (*4.6*)) they have different origin as Eq. (*4.4*) refers to. They are the result of different combinations of underlying step rates (J_1 and J_2). In other words, the cause

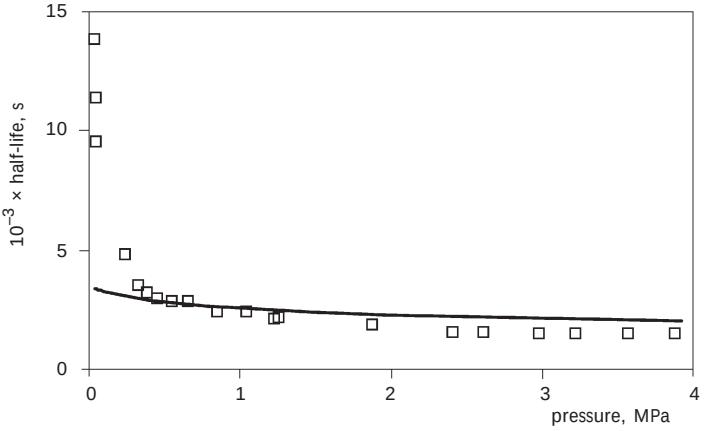

FIG. 2

Dependence of the reaction half-life on the initial pressure of nitrous oxide. Data points given by Hunter[42]. The line was calculated using the traditional mass-action equations (*4.10*) and (*4.11*) with $k_1 = 0.0002$, $k_2 = 0.000045$ and $k_3 = 0$ neglecting reverse reaction rates

of distinction is the transformation (*4.4*) of reaction rates into component rates. Although the reaction rates have the same form their coefficients are generally different. Whereas this explanation is quite plausible in phenomenological (macroscopic) description, interpretation on molecular level would deserve further study. At this moment it can be assumed that the difference in phenomenological rate coefficients (traditionally termed rate constants), which are necessary for adequate smoothing of experimental data, indicates that the employed scheme does not exactly reproduce events on the molecular level and is only their plausible macroscopic representation, i.e., the method can indicate whether we have a reaction mechanism or network.

TABLE II
Rate coefficients in Eqs (*4.5*) and (*4.6*) used in numerical simulation (Fig. 3)

k'^{1}_{0010}	k'^{2}_{0010}	k'^{1}_{0110}	k'^{2}_{0110}	k'^{1}_{0200}	k'^{2}_{0200}
8.415×10^{-5}	-8.585×10^{-5}	-8.415×10^{-5}	-8.585×10^{-5}	8.500×10^{-5}	-8.500×10^{-5}

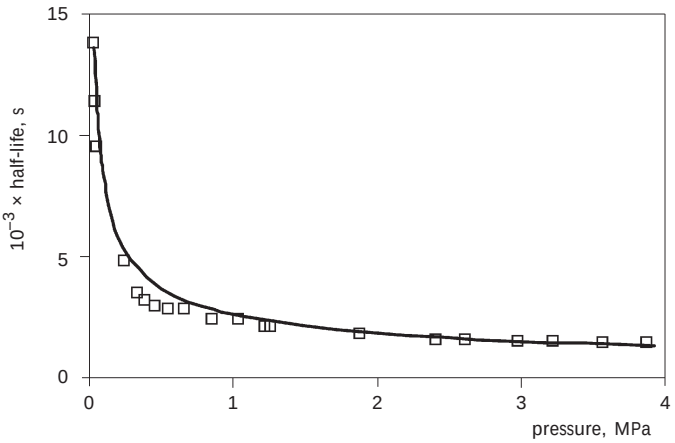

FIG. 3
Dependence of the reaction half-life on the initial pressure of nitrous oxide. Data points given by Hunter[42]. The line was calculated with the new equations (*4.5*) and (*4.6*) neglecting reverse reaction rates; rate coefficients are given in Table II

5. REACTION MIXTURE CONTAINING N_2O, N_2, O_2, O, NO, NO_2

This mixture follows from many published works and is considered as general in the review by Bamford and Tipper[38] if we consider the general species M given in them to be one from the set N_2O, N_2, O_2 or NO. M can symbolize also an inert gas but this has no substantial impact on the following discussion.

In this mixture, four independent reactions are possible. Let us select the following quaternary.

1. $N_2O = N_2 + O$
2. $N_2O + O = O_2 + N_2$
3. $N_2O + O = 2\ NO$
4. $O + NO = NO_2$ (*5.1*)

Approximation by the second-degree polynomial leads to the following rate equation.

$$\begin{aligned} J = {} & \boldsymbol{k}_{100000}(c_{N_2O} - K_1^{-1} c_{N_2} c_O) + \boldsymbol{k}_{101000}(c_{N_2O} c_{O_2} - K_I c_{NO} c_{NO_2}) + \\ & + \boldsymbol{k}_{100100}(c_{N_2O} c_O - K_3^{-1} c_{NO}^2) + \boldsymbol{k}_{100010}(c_{N_2O} c_{NO} - K_1^{-1} K_4^{-1} c_{N_2} c_{NO_2}) + \\ & + \boldsymbol{k}_{011000}(c_{N_2} c_{O_2} - K_2 K_3^{-1} c_{NO}^2) + \boldsymbol{k}_{000110}(c_O c_{NO} - K_4^{-1} c_{NO_2}) + \\ & + \boldsymbol{k}_{000101}(c_O c_{NO_2} - K_{II} c_{O_2} c_{NO}) + \boldsymbol{k}_{000200}(c_O^2 - K_1 K_2^{-1} c_{O_2}) \end{aligned} \quad (5.2)$$

where $K_I = K_1^{-1} K_2 K_3^{-1} K_4^{-1}$ and $K_{II} = K_1 K_2^{-1} K_4$. The corresponding scheme is as follows.

1.* $N_2O = N_2 + O$
2. $N_2O + O_2 = NO + NO_2$
3.* $N_2O + NO = N_2 + NO_2$
4.* $O + NO = NO_2$
5.* $O + NO_2 = O_2 + NO$
6.* $2\ O = O_2$

$$7.^{*}\quad N_2O + O = 2\ NO$$

$$8.\quad N_2 + O_2 = 2\ NO \qquad (5.3)$$

The second-order steps reported by Bamford and Tipper[38] are recovered (marked by asterisk) with two steps more. The missing third-order steps of Bamford and Tipper would appear in the third-degree polynomial approximation, which is not discussed here.The traditional mass-action kinetics corresponding to steps (*5.1*) is thus neither second- nor third-degree polynomial approximation to the general rate function (*2.1*).

All selected independent steps (*5.1*) except the second one appear in the list (*5.3*). Remember that its rate is nevertheless contained in the vector ***J*** and its equilibrium constant in the rate equations (5.2), i.e., this step was not actually excluded from kinetic description. In fact, this step is a result of subtraction of the step (*5.3.8*) from the step (*5.3.7*). The thermodynamic method just shows how the rates of independent reaction steps can be "translated" into the rates of more and dependent steps forming a scheme suitable for description of chemical changes in the reacting mixture under consideration. This is a unique feature of the method – not only that it operates just on independent reactions but it does not exclude other steps from affecting reaction kinetics and even shows how the dependent step may influence the rates of selected independent steps and, consequently, the overall reaction kinetics. It is also worth noting that the concentration term directly corresponding to the mass-action expression for the step (*5.1.2*) has ostensibly "disappeared" from Eq. (*5.2*) just due to the equilibrium condition, i.e., just due to the requirement that the approximating rate polynomial should vanish at equilibrium. Details of this procedure are explained in section 6.

Four components of vector ***J*** in (*5.2*) are the rates of selected independent reactions (*5.1*), i.e., J_i. If we want to obtain just the classical rate equations for the scheme (*5.3*) with only irreversible steps, let us select the values of polynomial coefficients (rate constants) in Eq. (*5.2*) as given in Table III and set all the other coefficients equal to zero. It can be easily verified that the resulting formation rates

$$J^{N_2O} = -J_1 - J_2 - J_3$$

$$J^{O} = J_1 - J_2 - J_3 - J_4$$

$$J^{N_2} = J_1 + J_2$$

$$J^{O_2} = J_2$$

$$J^{NO} = 2J_3 - J_4$$

$$J^{NO_2} = J_4 \qquad (5.4)$$

are in accord with this tradition. Consequently, the traditional mass-action rate equations are, in this reacting mixture, special cases of the second-degree approximating polynomial to the general rate function (*2.1*).

6. FUNCTIONING OF THE METHOD

In this section explanatory notes on how the method works are given. The method is rooted in a strict mathematical logic. For instance, in the reacting mixture N_2O, N_2, O_2 the monomolecular step (decomposition of nitrous oxide) could not appear as the atomic oxygen was not present in the list of components. Therefore, the rate equations could not have the form of sum of terms with first and second powers of the nitrous oxide concentration, i.e., sum of the first- and second-order steps with respect to N_2O.

Why, for instance, in the reacting mixture N_2O, N_2, N_2O, O does not appear the step $2\ N_2O = 2\ N_2 + O_2$ in the resulting polynomial and the other, (*4.3.2*), not included among the independent steps, has "appeared" in the scheme (*4.3*)? The full approximating second-degree polynomial is in this case as follows (to simplify notation, vector components are not distinguished by special indices).

$$J = k_{0000} + k_{1000}c_1 + k_{0100}c_2 + k_{0010}c_3 + k_{0001}c_4 +$$
$$+ k_{2000}c_1^2 + k_{1100}c_1c_2 + k_{1010}c_1c_3 + k_{1001}c_1c_4 + k_{0110}c_2c_3 +$$
$$+ k_{0101}c_2c_4 + k_{0011}c_3c_4 + k_{0200}c_2^2 + k_{0020}c_3^2 + k_{0002}c_4^2 \qquad (6.1)$$

TABLE III
Specific selection of rate coefficients in Eq. (*5.2a*), ($k_i > 0$, $i = 1, 2, \ldots, 8$)

k'^{1}_{100000}	k'^{1}_{101000}	k'^{2}_{101000}	k'^{3}_{101000}	k'^{4}_{101000}	k'^{3}_{100100}	k'^{1}_{100010}	k'^{4}_{100010}
k_1	k_2	$-k_2$	k_2	k_2	k_7	k_3	k_3
k'^{2}_{011000}	k'^{3}_{011000}	k'^{4}_{000110}	k'^{1}_{000101}	k'^{2}_{000101}	k'^{4}_{000101}	k'^{1}_{000200}	k'^{2}_{000200}
$-k_8$	k_8	k_4	$-k_5$	k_5	$-k_5$	$-k_6$	k_6

In the next step when the equilibrium relations are applied, only those polynomial terms (powers of concentrations or their products) "survive" that appear at least twice and with different coefficients. Such associated terms may appear in the polynomial only after substitutions from the expressions for equilibrium constants, (*2.4*).

In our example of the independent reactions (*4.1*) the following relations for the equilibrium constants are used.

$$K_1 = c_2^{eq} c_4^{eq} / c_3^{eq}; \quad K_2 = c_1^{eq} c_4^{eq} / c_2^{eq} c_3^{eq} \tag{6.2}$$

From them, e.g., concentrations of the first and third component are expressed.

$$c_3^{eq} = K_1^{-1} c_2^{eq} c_4^{eq}; \quad c_1^{eq} = K_2 c_2^{eq} c_3^{eq} (c_4^{eq})^{-1} = K_1^{-1} K_2 (c_2^{eq})^2 \tag{6.3}$$

Substituting them into the equilibrium (vanishing) polynomial (*6.1*), a polynomial with two variables only results. The term which would correspond to the forward step 2 N_2O = 2 N_2 + O_2, i.e., $k_{0020}(c_3^{eq})^2$, appears only once. Further, the term corresponding to its reverse direction does not appear at all (it would require a third-order polynomial). Therefore, the term $k_{0020}(c_3^{eq})^2$ can vanish in the equilibrium polynomial only by setting k_{0020} = 0 and that reaction step "disappears" from the final kinetic equation.

On the contrary, the term corresponding to the forward direction of the independent reaction (*4.1.1*), i.e., $k_{0010} c_3^{eq}$, can be combined in the equilibrium polynomial with the term $k_{0101} c_2^{eq} c_4^{eq}$, because due to (*6.3*), the following identity is valid.

$$k_{0010} c_3^{eq} = k_{0010} K_1^{-1} c_2^{eq} c_4^{eq} \tag{6.4}$$

Consequently, in the equilibrium polynomial the combined term $(k_{0010} K_1^{-1} + k_{0101}) c_2^{eq} c_4^{eq}$ appears, which after application of the equilibrium condition (vanishing rate regardless of particular values of equilibrium concentrations), leads only to the following requirement

$$k_{0010} K_1^{-1} = -k_{0101} \tag{6.5}$$

and not to vanishing of the whole term, i.e., vanishing the step (*4.1.1*) from the resulting reaction scheme.

For similar reasons a new reaction step not included in the set of selected independent reactions, viz. (*4.3.3*), appears in the final rate equation. Thus, the reaction (*4.3.3*) is a consequence of the terms $k_{1000} c_1$ and $k_{0200} c_2^2$ in the

approximating polynomial, which can be combined in the equilibrium due to Eq. (*6.3*) as follows.

$$(k_{1000}K_1^{-1}K_2 + k_{0200})(c_2^{eq})^2 \qquad (6.6)$$

The requirement for the vanishing equilibrium polynomial in any equilibrium does not call for vanishing k_{1000} or k_{0200}. Other polynomial terms which do not have suitable counter-terms, e.g., $k_{0100}c_2^{eq}$; $k_{0002}(c_4^{eq})^2$; $k_{1100}c_1^{eq}c_2^{eq}$ may fulfill the general equilibrium condition only by vanishing their coefficients, i.e., $k_{0100}; k_{0002}; k_{1100}$, and do not appear in the final kinetic equation.

Though there is some freedom in the selection which equilibrium concentrations are expressed from definitions of equilibrium constants (*2.4*), the resulting relationships of polynomial coefficients like (*6.5*) are invariant to this selection, i.e., identical schemes follow. Because, as explained above, also the selection of independent reactions has no influence on the form of the rate polynomial, rate equations and resulting scheme can be varied just by varying the polynomial degree.

Functioning of the method can be summarized in this way. Terms of various orders in the approximating polynomial represent reaction steps of the corresponding molecularity (or reaction order). Only those terms ("reactions") are retained in the final kinetic equation, that are somehow interconnected through the equilibrium constants of the selected independent reactions. The terms which are not linked with the independent reactions vanish automatically.

7. SUMMARIZING DISCUSSION

Traditional mass-action rate expressions and reaction mechanisms (networks) are included within outcomes of the presented thermodynamic method. Usually, they are simplified forms of functional approximation that forms the core of the thermodynamic approach. The method further offers more general rate expressions and corresponding reaction schemes which can improve kinetic and thermodynamic description and understanding of a given reacting system. Briefly, the thermodynamic method proposes complete plausible rate equations and reaction steps for given reactants, products, intermediates, and selected maximum reaction order (or molecularity). Experiments or (quantum chemistry) calculations can then select the best or right order and can further simplify reaction rate and scheme.

The example of nitrous oxide decomposition perhaps clearly illustrated that the investigated methodology adds general framework and a new potential to the traditional design of rate equations and schemes. Rational thermodynamics sheds a new, "thermodynamic" light on what has been and is done by generations of kineticists and gives hints how to do it in a way consistent with non-equilibrium thermodynamics. Thermodynamics is not merely used to test the thermodynamic consistency of proposed rate equations but directly suggests consistent rate equations that include also a reaction mechanism or network. The example clearly shows that traditional mass-action law kinetic equations are usually only special, simplified cases of low-order polynomial approximations to the general rate function that results from rational thermodynamics as a proved function.

The method starts only with the list of (experimentally determined or by calculations confirmed) constituents of a reacting mixture and operates only with so many reactions as corresponds to the number of independent reactions. Polynomial-like rate equations are derived the complexity of which can be varied by varying the degree of polynomial employed. In most practical situations second- or third-degree polynomial should be sufficient and recommended. Relating the results to kinetic tradition and kinetic way of thinking, individual terms of resulting polynomial are interpreted as classical mass-actiontype rate expressions and a reaction scheme, necessary for description of kinetics in the reacting mixture of interest, then naturally follows. One of the most interesting and important consequences is that not only the (mathematically, i.e., "thermodynamically") independent reactions may appear in the resulting rate equation and scheme. Thus the method naturally and inherently resolves the question on the significance of thermodynamically dependent reaction steps in kinetics of a reaction. The method clearly shows that reactions, which may not be "thermodynamically" important, i.e., which are not included among the independent reactions, may still be important for kinetic description and may be a part of assumed reaction scheme and designed rate equations. The correct role of (thermodynamically) independent reactions in chemical kinetics is clarified – although these reactions control the formulation of rate equation, the other reactions are not totally excluded from kinetic effects.

The presented method does not construct rate equations for individual reactions which include only those components (substances), that take part in the particular step as is the case of traditional mass-action approach. Therefore it can lead to some paradoxes in kinetic equations. For instance, a reaction may seemingly "disappear" from its own rate equation (cf. the

rate equation (*5.2*) for the reaction (*5.1.2*)) or, on the contrary, some other reactions may "appear" in its rate equation (cf. the rate equation (*3.3*) for the reaction (*3.1*)). The latter outcome points to a potential influence of some reaction (in other words, of "foreign" components) on kinetics of some other reaction or to affecting reaction rates by "inerts". This is not unknown even in the traditional kinetics[14] but not motivated or even proved by the classical theories and rarely used in practice. The cause of these "external effects" lies in the rational thermodynamic proof that the rate of any reaction may be a function of concentration of any component from the reacting mixture.

The main cause of final modification and simplification of initial approximating polynomial is equilibrium, viz. its general validity and the existence of the equilibrium constant. This stresses the power of equilibrium state even in the non-equilibrium theories. Indeed, equilibrium is the final state that also a non-equilibrium system should reach at last. In this work, other modifications guided by an effort to arrive at some specific rate equations proposed for the selected example reaction were made. They may naturally lead to concentration-dependent rate "constants". It is worth mentioning that the presented method enables also deriving rate equations in the form of a known rational algebraic function, e.g. in enzyme kinetics or Lindemann's treatment of monomolecular reactions. Exemplification is outside the scope of this paper and will be given in a future work.

The method enables exploitation of ample thermodynamic databases; it does not operate with "reverse" rate constants – they are, in fact, given by combinations of equilibrium constants which can be calculated from thermodynamic data. This further reduces the number of parameters that should be estimated from experimental data. The method thus really put together kinetics and thermodynamics.

It should be stressed that this method does not take the philosophy "make measurements on the overall kinetics of the major species in a system and then try to infer some reaction schemes from these data" and need not be limited to phenomenological approaches only. Even the results of detailed experiments made to determine all intermediates and thus to elucidate the resulting reaction scheme or a set of elementary steps formulated from quantum chemical calculations should conform to thermodynamic laws and permanence of atoms.

Usually no mechanisms or networks are directly measured. Only concentration profiles of detected constituents are obtained and a mechanism or network is inferred from them using information on constituent structures, chemical knowledge or results of molecular modeling. If kinetic equations

formulated from the assumed reaction scheme fit the data well, the scheme is considered to be acceptable and sufficient. The discussed method offers another way to do this and to do it in reverse order than traditionally – the rate equation is formulated first and a scheme follows just from it. And all what is needed from experiments is to find all constituents (including intermediates) of a reacting mixture. The approaches presented by Ross[2] also work with the identification of "all" individual chemical species within a reacting mixture but focus on performing and analyzing special experiments which should reveal connectivities or correlations within the reacting system and, consequently, the reaction scheme. The presented approach, on the other hand, provides a general and thermodynamic framework for deducing reaction rates and schemes that needs "only" a list of the species. Both approaches can be combined – e.g., schemes proposed by the latter can be tested for realistic connectivities or schemes deduced by the former may be confronted with the described consequences of permanence of atoms and thermodynamic consistency.

8. CONCLUSIONS

Continuum (rational) thermodynamics shows how one of the principal laws of nature – conservation of mass – is projected into rate equations and schemes. Kinetic consequences are close to the traditional mass-action approach that is thus put within the framework of non-equilibrium thermodynamics and its potential for description of kinetic data is substantially extended. Traditional kinetic mass-action law, that has been shown to be limited to reacting mixtures of fluids with linear transport properties, gives rate equations that are only simplified forms of a low-order polynomial approximation to the general mass-action rate function proved by continuum thermodynamics. The example of nitrous oxide decomposition showed that the method naturally and inherently contains many otherwise specific hypotheses made to explain experimental outcomes of specific reaction kinetics and that the proposed new, non-traditional rate equations correspond to experimental data better than the traditional mass-action law.

The described thermodynamic method does not need an *a priori* mechanism statement. On the contrary, it proposes mechanisms (or networks) directly and clearly and naturally shows that the mathematically-thermodynamically sufficient reaction steps may not be sufficient for the description of kinetics. The method also provides an inherent indicator whefher the proposed scheme that gives a good fit of experimental data is only a plausible macroscopic representation (a "reaction network") of the

true processes occurring on the molecular level. The method enables the direct use of vast data amounts from thermodynamic databases in kinetic equations.

More complex rate equations than usual in the mass-action kinetics can be derived; this just means that the method alerts that there can be other influences on the rate of particular reaction than usually expected in traditional kinetics. For instance, the influence of some other components of a reacting mixture than those directly taking part in the reaction step. After all, the nitrous oxide decomposition discussed here is a nice example as very decomposition step is often written not as $N_2O \rightarrow N_2 + O$ but as $N_2O + M \rightarrow N_2 + O + M$, where M can be any constituent of reacting mixture.

The described method gives rules or guidance how to interpret kinetic data within the framework of mechanisms or networks and may improve our design and understanding of necessary and sufficient reaction schemes. It reverses the common practice of scheme deduction – first the rate equation is constructed and just from it the scheme is inferred. The method is firmly rooted in mathematics and thermodynamics and in experiments that have revealed all constituents of a reacting mixture. It does not preclude simplification of derived equations, which is substantiated by experimental results or chemical insights.

It is hoped that from the presented example of a relatively well understood and studied reaction, the kinetic community can get an idea on functioning, potential and outcomes of the rational thermodynamic approach and will help to further elaborate testing and evaluating its application in chemical kinetics and in particular kinetic data interpretation. Perhaps any proposed rate equation or scheme should be tested, at least, for consistency with permanence of atoms and irreversible thermodynamics as elaborated within the approach presented in this work.

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