NONLINEAR THERMODYNAMICAL STUDIES OF HOMOGENEOUS CHEMICAL KINETIC SYSTEMS

By

S. LENGYEL* and I. GYARMATI

* Central Research Institute for Chemistry,
Hungarian Academy of Sciences, Budapest

Institute of Physics, Technical University, Budapest

Received April 17, 1980

Introduction and Preliminaries

It is often asserted that the linear theory [3—10] of irreversible thermodynamics, the foundations of which were laid by ONSAGER [1] and CASIMIR [2], does not adequately represent irreversible phenomena in systems far from equilibrium. Such assertions are correct if we consider the linear flux-force constitutive equations of the original Onsager theory, i.e., equations

$$I_i = \sum_{k=1}^{f} L^0_{ik} X_k \quad \text{with} \quad L^0_{ik} = L^0_{ki}, \quad (i, k = 1, 2, \ldots, f) \tag{1}$$

where $L^0_{ik} = L^0_{ki}$ are the Onsager reciprocal relations (ORR) and L^0_{ik} are constant coefficients. However,if we make allowance for the so-called quasilinear generalisation of the theory proposed by GYARMATI [11—15] (for further references see [15]) according to which the conductivity coefficients L_{ik} may depend, for example, on the intensive thermostatic state variables $\Gamma_1, \ldots, \Gamma_f$, then the constitutive equations

$$I_i = \sum_{k=1}^{f} L_{ik}(\Gamma_1, \ldots, \Gamma_f) X_k \tag{2}$$

with the ORR-s in the form $L_{ik}(\Gamma_1, \ldots, \Gamma_f) = L_{ki}(\Gamma_1, \ldots, \Gamma_f)$ and with the Gyarmati supplementary reciprocal relations

$$\frac{\partial L_{ik}(\Gamma_1, \ldots, \Gamma_f)}{\partial \Gamma_j} = \frac{\partial L_{ki}(\Gamma_1, \ldots, \Gamma_f)}{\partial \Gamma_j}, \quad (j = 1, 2, \ldots, f) \tag{3}$$

warrants good approximation for example in the case of transport processes. On the other hand, there are only very rare cases of transport processes where currents I_i nonlinearly depend on forces X_i, i.e.,

$$I_i = f_i(\Gamma_1, \ldots, \Gamma_f, X_1, \ldots, X_f, X_1^2, \ldots, X_f^2, \ldots) \tag{4}$$

For illustration, heat conduction in anisotropic solids should be mentioned. Since over a century we have known that Fourier's law for anisotropic solids, i.e.

$$(\mathbf{I}_q)_\alpha = - \sum_{\beta=1}^{3} \lambda^0_{\alpha\beta} (\nabla T)_\beta; \quad \lambda^0_{\alpha\beta} = (\text{const})_{\alpha\beta} \tag{5}$$

which is a special case of equation (1), is no good approximation in the case of some materials, even if temperature gradient ∇T is equal to a few degrees per cm. In equation (5) $(\mathbf{I}_q)_\alpha$ is the αth component of the heat current density and $\lambda^0_{\alpha\beta}$ are the elements of heat conductivity tensor. On the other hand, the constitutive equations of the quasilinear theory, i.e.,

$$(\mathbf{I}_q)_\alpha = -\Sigma\lambda_{\alpha\beta}(T)(\nabla T)_\beta \quad (\alpha = 1, 2, 3) \tag{6}$$

with the Onsager reciprocal relations $\lambda_{\alpha\beta}(T) = \lambda_{\beta\alpha}(T)$ and the Gyarmati supplementary reciprocal relations

$$\frac{\partial\lambda_{\alpha\beta}}{\partial T} = \frac{\partial\lambda_{\beta\alpha}}{\partial T}, \quad (\alpha, \beta = 1, 2, 3) \tag{7}$$

warrant practically exact description even in the case of the highest values of the temperature gradient. The exactness of description depends on how the $\lambda_{\alpha\beta}(T)$ functions are known experimentally. In any case, we do not know heat conduction phenomena where the description necessarily involved strictly nonlinear constitutive equations of the form [12, 13]:

$$I_q = -[\lambda(T) + L(T)(\nabla\mathbf{T})^2 + \ldots]\nabla\mathbf{T} = \lambda'(T, \nabla\mathbf{T})\nabla\mathbf{T} \tag{8}$$

Here for the sake of simplicity, isotropic material was considered, and $\lambda' = \lambda(T) + L(T)(\nabla T)^2$ is the heat conductivity coefficient depending on both T and ∇T.

Without going into details, we would mention here that some two decades ago Gyarmati [16, 17] and Li [18, 19] laid the foundations of a nonlinear theory, which was completed later by several authors (Gyarmati [12], Verhás [14], Edelen [20, 21] and recently Keller [22]). Thus, recently we have at our disposal a nonlinear theory of thermodynamics, which is mathematically complete, as e.g., the linear theory or its quasilinear form. This old nonlinear theory is based on the generalized reciprocity relations (GRR)

$$\frac{\partial I_i}{\partial X_k} = \frac{\partial I_k}{\partial X_i} \quad (i, k = 1, \ldots, f) \tag{9}$$

formulated independently by Gyarmati and Li. However, up to this day we do not know of any acceptable derivation or immediate experimental proof of these relations. It should be noted that distinction must be made between the GRRs (9) consituting the foundations of the strictly nonlinear theory and the supplementary reciprocal relations of form (3), or in the special case of anisotropic heat conduction of form (7). The validity of latter is beyond question. It should also be emphasized that in the case of transport processes, terms of higher than linear degree are only very seldom required in the polynomic type constitutive equations

$$I_i = \sum_k L_{ik} X + \frac{1}{2!} \sum_{k,j} L_{ikj} X_k X_j + \dots + \sum L_{ikjlm\dots} X_k X_j X_l X_m + \dots \tag{10}$$

proposed by Gyarmati and Li as a direct generalization of the Onsager theory. It should be remarked here that from the aspect of physics, all "modern" nonlinear theories lack seriousness in which the authors propose the use of constitutive functionals. As a matter of fact, whatever constitutive functionals — meeting rational arguments and postulates — are proposed for a nonlinear theory, introduction of these functionals into a physical theory is equivalent to the implicit resignation to prove the theory experimentally. Theories based on constitutive functionals have the advantage today that they cannot be experimentally disproven and will have the disadvantage tomorrow that they cannot be experimentally proven.

Returning to the physical reality, we mention here that though the ORR-s are in many cases experimentally proven and their validity is beyond doubt, in certain cases their verification involves elaborate techniques and is very difficult. The brilliant papers of MILLER [23, 24] should be referred to in this context. Taking his work into account, we may see that in the case of anisotropic heat conduction it is not sufficient to prove experimentally the ORR-s

$$\lambda_{xy} = \lambda_{yx}, \quad \lambda_{xz} = \lambda_{zx}, \quad \lambda_{yz} = \lambda_{zy}, \tag{11}$$

between the coefficients of the constitutive equation (6). This had already been performed by SORET [25, 26] and VOIGT [27] around the turn of the century. In addition, according to the GRR (9), one has to prove also the symmetries

$$L_{xxxy} = L_{yxxx}, \quad L_{xxxz} = L_{zxxx}, \quad L_{xyxy} = L_{yxyx}, \quad \text{etc.} \tag{12}$$

of the fourth order conductivity tensor $L_{\alpha\beta\gamma\delta}$. Those who are familiar with the experimental difficulties involved may be sure that the experimental verification of relations (12), which in this special case represent the Gyarmati—Li GRR, is a lost case. Moreover, even the experimental existence of the tensor $L_{\alpha\beta\gamma\delta}(T)$ is doubtful.

It is clear from the foregoing that in the case of transport processes we can hardly expect the experimental verification of the relatively simple nonlinear thermodynamic theory proposed at the end of the fifties [16, 18]. This seems to be so, in spite of the fact that this theory is a direct generalization of the experimentally proven linear Onsager theory. Nevertheless, chemical reactions are irreversible processes where the rate functions of the Guldberg—Waage form [28—30] may enable us to prove the reality of the above mentioned nonlinear thermodynamic theory. We hope that the consistency of this theory with the Guldberg—Waage kinetics will be shown some day, which generalizes the experience on thousands of reactions, and think that this will much contribute to the acceptance of the Gyarmati—Li theory.

This consistency is both theoretically and practically important also from the aspect of reaction kinetics. If we can show this consistency, then the whole phenomenological theory of chemical reactions will become a special but organic branch of non-equilibrium thermodynamics in the same way as the theory of chemical equilibria has become a special chapter of thermostatics as a result of Gibbs' work. From the practical point of view, on the other hand, the description in non-equilibrium thermodynamics not only offers an alternative description of chemical reactions but can complete the Guldberg—Waage theory. We think that reaction kinetics describes only the concentrations as a function of time but the reaction heats involved in the reaction, i.e., the energetics are not included in the description. In non-equilibrium thermodynamics this inclusion is quite natural, moreover, if the equivalency of both theories can be assumed, then stationary states, stability and evolution of open kinetic systems may become objects of exact studies by means of adequate principles and theorems of non-equilibrium thermodynamics [8, 12]. Since the above problems and their solutions are both theoretically and practically of greatest importance in chemical kinetics as well as in their biochemical and biological application, we think that the consistency of nonlinear thermodynamics and chemical kinetics is a problem of primary importance in modern science.

Before turning to the question of the consistency of nonlinear thermodynamics and reaction kinetics, we would mention that even the relation of the linear Onsager theory to the linearized form of the Guldberg— Waage theory is not entirely clarified. This is surprising, all the more, as it was a reaction kinetical example — the monomolecular triangle reaction — used by ONSAGER [1] to illustrate the ORR-s as early as 1931. In spite of this, it can be seen from monographs on non-equilibrium thermodynamics [3—10] and other works [31] that the thermodynamical evolution of reaction kinetics has not been completed; not even in the linear domain. Adequate and up to now the most complete treatments were presented by OLÁH [32] and SCHUBERT [33], which — although not widely known in the international literature — show the insufficiencies of the theory. We have the following insufficiencies in mind. a) The theory is not systematically elaborated and a wide application to chemical kinetics is lacking. b) The theory is not much more than linear transformation between fluxes and forces (see e.g. [7]). Occasionally, misinterpretations of the transformation occur, wich are due to inadmissible generalization and not sufficiently careful application [34] of the well established Meixner transformation theorems (see e.g. [7]). c) The equations of motion for thermodynamic forces (i.e., affinities in reaction representation) found already in 1957 [16, 17] have not been applied, though they could be used to describe the evolution of the affinities (or reaction heats) in the course of time. This is a priori impossible in pure reaction kinetics. These facts justifie the elaboration of a complete thermodynamic theory of reaction kinetics in its linear and nonlinear forms.

Unfortunately, it is generally believed that linear thermodynamics is not a good approximation in the description of chemical reactions with the exception of the immediate vicinity of equilibrium. Considering the above outlined points, however, the elaboration of a complete linear theory and its application to chemical reactions is thought to be not as useless as generally believed. There are two facts to be pointed out here. In relaxation kinetics established in the sixties by EIGEN and coworkers [35], up to this date, almost exclusively linear approximation has been applied with much success [36]. Since, however, it was not possible for authors working in relaxation kinetics to apply a linear thermodynamic theory to chemical kinetics, they had no other choice but to find theorems and equations, often in an incomplete form, which could have been found automatically and in complete form in the linear thermodynamic theory of reaction kinetics.

There are further practical reasons for the elaboration and application of a complete form of the linear thermodynamic theory of reactions. The study of complex reactions shows that although it is simple to find the simultaneous system of the corresponding Guldberg—Waage equations, which are generally nonlinear differential equations, their solutions cannot be found in analytical form. Those treating such problems either resort to methods of mathematical approximation [37] or use more or less reasonable simplifications of the initial system of equations. Among these, the principle of quasistationarity (Bodenstein) and the hypothesis of quasiequilibrium should be mentioned here, by which linearization or at least significant simplification can be managed. Such principles of reduction and their effect is always of ad hoc character. Moreover, in some cases such reductions of the original nonlinear equations are so drastic that the solution is a misinterpretation of the kinetics studied. Often a truer picture of the kinetics could be obtained by direct use of the linear thermodynamical theory of reaction kinetics and by exact solution of the linear equations than by the ad hoc and drastic methods used in the solution of certain reduced forms of nonlinear kinetic equations.

To illustrate the situation, let us assume that we could show the consistency of nonlinear thermodynamics and nonlinear theory of chemical kinetics. In this case, instead of the Guldberg—Waage form of the kinetic equations the consistent differential equations of the nonlinear thermodynamic theory have to be solved. Those underestimating the linear theory of thermodynamics do not benefit by the nonlinear theory, even if it is assumed to be consistent with nonlinear reaction kinetics, since it is equally difficult to solve nonlinear differential equations, irrespective of the kinetic or thermodynamic content of these equations.

Let us now turn to the question of consistency of nonlinear thermodynamics and nonlinear chemical kinetics. Since 1963 confusion has prevailed in this domain. Therefore, first the following three questions must be clarified:

By whom was the GRR proposed in the form (9)? When was this proposed? In what sense was it proposed? These questions are important because without deeper knowledge of the literature some authors use relations (9) in different senses and various forms. It was perhaps Denbigh who in 1951 first used relations (9) (see [4] page 30), although he used these relations only as alternative forms of the ORR of the linear theory. No mention was made, however, according to which he would have postulated the validity of equations (9) beyond the linear domain.

Starting with the obscure expression

$$dS = \sum_i X_i dx_i \tag{13}$$

of non-equilibrium entropy change, GIBERT [38] in 1953 derived equations (9) using certain mathematical manipulations. For the moment it is not important to show the incorrectness of this derivation, since there is up to now no perfectly correct derivation. We wish to point out here that Gibert's only aim was to derive the ORR-s from macroscopic thermodynamic principles i.e., without assuming any microscopic principle or hypothesis. No reference has been made in his paper to the assumption that relations (9) might be valid for nonlinear constitutive equations. Hence, Gibert did not propose any nonlinear constitutive equation and has not elaborated any nonlinear theory.

The GRR-s are also assigned to PÉNÉLOUX [39] and DODÉ [40]. Dodé seems to have set as his aim the specialization of Gibert's results to chemical reactions. In this very qualitative paper we find only two equations

$$\mathrm{d}S' = \sum_i \frac{A_i}{T}\,\mathrm{d}\xi_i = \sum_i F_i\,\mathrm{d}\xi_i \quad \text{and} \quad \left(\frac{\partial \xi_i}{\partial F_k}\right) = \left(\frac{\partial \xi_k}{\partial F_i}\right) \tag{14}$$

where dS' is the entropy created by the chemical reactions, A_i and ξ_i are affinity and degree of advancement of reaction i. He regarded the second equation (14) as Gibert's reciprocitiy relation, although it is a Maxwellian. Consequently, Dodé's paper cannot be regarded as publication of a nonlinear thermodynamic theory. Péneloux (1954) in the special case of chemical reactions derived the ORR-s in the form $RL_{ik} = RL_{ki}$ (R is the gas constant) by questionable manipulations. In his second paper (1957) he publishes the relation

$$\frac{\partial I_i}{\partial A_k} = \frac{\partial I_k}{\partial A_i} \tag{15}$$

for chemical reactions. Here I_i, I_k are reaction rates and A_i, A_k affinities. However, he does not propose any nonlinear theory and cannot be regarded as a pioneer in nonlinear thermodynamics, not even in the special case of reaction kinetics.

In 1962 RYSSELBERGHE [41, 42] became aware of the fact that validity of the Péneloux reciprocity relations (15) may be considered as independent of the linear domain of reaction kinetics. He postulated their validity in the case of the following nonlinear equations

$$\begin{aligned} I_1 &= L_{11}A_1 + L_{12}A_2 + L_{111}A_1^2 + L_{112}A_1A_2 + L_{122}A_2^2 \\ I_2 &= L_{21}A_1 + L_{22}A_2 + L_{211}A_1^2 + L_{212}A_1A_2 + L_{222}A_2^2 \end{aligned} \qquad (16)$$

Combination of equations (15) and (16) leads to the ORR $L_{12} = L_{21}$ and, in addition, to the reciprocal relations of higher order of the form

$$L_{112} = 2L_{211}, \quad L_{212} = 2L_{122} \qquad (17)$$

Here some observations have to be made.

We may establish that it was Rysselberghe who first proposed nonlinear constitutive equations between reaction rates and affinities and he was the first to regard relations (15) as valid for the nonlinear domain of chemical kinetics. Therefore, it is justified to call equation (15) the "Rysselberghe generalized reciprocity relation" (RGRR).

The theory proposed by Gyarmati and Li (1957—1962) was more general and more carefully elaborated than the Rysselberghe theory, and the former was known to the author of the second. Therefore, the quastion could be raised: is the second theory an a posteriori specialization of the first? However, this is not the case. In the Gyarmati—Li theory there is no restriction postulating that in its application to reaction kinetics the affinities should be regarded as thermodynamic forces in the nonlinear constitutive equations. Consequently, the Rysselberghe theory cannot be regarded as a special reaction kinetic form of the older and more general Gyarmati—Li theory. In other words, we must not regard constitutive equations (10) and GRR(9) in the special case of chemical kinetics as relations from which, with substitution of $X_i \equiv A_i$ we arrive at the theory of Rysselberghe. In spite of its similarity in form, the Rysselberghe theory differs from the Gyarmati—Li theory and is narrower than the latter not only because it is proposed only for chemical reactions but rather because it is based on the assumption that affinities are the real thermodynamic forces also in the nonlinear domain!

RYSSELBERGHE [42] applied his theory to triangle reactions and derived, in addition to the Wegscheider equation, further three relationships as a result of the symmetries (17). In 1965—1966 WEI and ZAHNER pointed out [43] that Rysselberghe's derivation of equation (15) is incorrect and, the

RGRR is in contradiction to experimental facts. For example, experiments show that in most monomolecular systems the reaction paths are curved, while from the existence of RGRR it would follow that all reaction paths are straight lines. Oláh arrived at similar conclusions according to which the afore-mentioned three relationships together with Wegscheider's equation represent four relationships between six rate constants, which is a restriction contradictory to experiment [32].

Analyses by Wei and Zahner as well as Oláh clarified in some particular cases that the Rysselberghe form of nonlinear thermodynamics is inconsistent with chemical kinetics. The Rysselberghe theory in its original and rough form could not be widely applied and proven. Therefore, BATAILLE, EDELEN and KESTIN's analysis [44] published in 1978, in which the authors treat the question of the consistency of chemical kinetics with nonlinear thermodynamics quite generally, is of fundamental importance. Their results may be summarized as follows.

1. The Marcelin—De Donder constitutive equations of chemical kinetics, which are equivalent to the Guldberg—Waage equations, satisfy the second law of thermodynamics.

2. The constitutive equations of chemical kinetics are, in linear approximation, consistent with the linear Onsager theory in the sense that in chemical kinetics the ORR-s are trivially satisfied.

3. In nonlinear approximation, in general, there is no consistency between the two theories. The RGRR-s are trivially satisfied in the case of some kinetic systems but they are not satisfied in other cases. However, we feel that the excellent analysis of Bataille, Edelen and Kestin is not a final conclusion concerning the question of consistency of nonlinear thermodynamics with chemical kinetics. Let us comment on the results of these authors.

Ad 1. According to Bataille, Edelen and Kestin, in linear approximation the ORR-s are trivially satisfied or, in other words, the matrix $\{L_{ik}\}$ of the chemical drag coefficients is in all cases diagonal. Evidently, this cannot be true, since Onsager in 1931 showed an example where the ORR is really satisfied. The real validity of the ORR is equivalent to the Wegscheider equation and the experimental verification of latter is a proof for the *real* satisfaction of the ORR [24].

Ad 2. In the first example of their paper, BATAILLE, EDELEN and KESTIN [44] considered $n - 1$ unimolecular reactions between n isomers in a closed system. However, in such systems kinetical coupling of reactions is a priori impossible both in the linear domain and in higher approximations. Therefore, this systems is no real example for the trivial satisfaction of the RGRR-s in the nonlinear domain.

In their second example the authors again considered monomolecular reactions among isomers but with a mechanism of the two reactions among four species specified by

$$[M_1] + 2[M_2] \rightleftharpoons [M_3] + 2[M_4]$$
$$[M_1] + 2[M_3] + [M_4] \rightleftharpoons 4[M_2] \tag{18}$$

They show that the RGRR-s are not satisfied in the nonlinear domain. Though this result is correct, we think the conclusion that nonlinear thermodynamics is inconsistent with chemical kinetics cannot be drawn from this, because the kinetic system (18) is not a system of elementary steps.

In conclusion our views on the problem are expressed as follows.

1. Detailed elaboration of the linear Onsager theory is much more important for chemical kinetics than is usually asserted. The conditions for trivial and those for real satisfaction of the ORR-s have to be clarified in general.

2. According to the analyses of Wei and Zahner, of Oláh as well as of Bataille, Edelen and Kestin, nonlinear thermodynamics based on the Rysselberghe reciprocity relations (15) in terms of reaction rates and affinities as fluxes and forces seem to be inconsistent with reaction kinetics. However, these analyses are either rather qualitative and restricted to special cases (Wei—Zahner, Oláh) or — although quantitative — the examples are not representative from the chemical point of view (Bataille—Edelen—Kestin).

This present paper has two aims: first, to present a final and general clarification of the conditions for trivial and real satisfaction of the Onsager relations in reaction kinetics; second, to analyze and illustrate the validity or invalidity of the RGRR by several real examples of chemical kinetic systems.

1. Reactions in a closed homogeneous system

Let us consider a closed homogeneous system of the K components $M_1, \ldots, M_K$ which participate in the R reversible reactions

$$\sum_{k'} \nu_{k'r} M_{k'} \rightleftharpoons \sum_{k''} \nu_{k''r} M_{k''}, \quad (r = 1, \ldots, R) \tag{1.1}$$

These equations represent the network and the chemism of reactions in the system. Here $\nu_{k'r} > 0$ denotes the stoichiometric coefficient of reactant $M_{k'}$, in reaction r and $\nu_{k''r} > 0$ denotes the stoichiometric ceofficient of product $M_{k''}$ in the same reaction. In the following, and in general, superscripts $'$ and $''$ will refer to reactants and products, respectively. The same component may or may not participate in two or more reactions. If component k does not participate in reaction r, then $\nu_{kr} = 0$. In equation (1.1) summation has to be extended over all reactants of reaction r on the left- hand side, and over all products of that reaction on the right-hand side. It is also usual to write equation (1.1) as

$$\sum_{k=1}^{K} \nu_{kr} M_k = 0 \text{ with } \nu_{kr} = \nu_{k''r} - \nu_{k'r} = \begin{cases} -\nu_{k'r} < 0 \text{ for reactants} \\ \nu_{k''r} > 0 \text{ for products} \end{cases} \tag{1.2}$$

where the stoichiometric matrix $\{\nu_{kr}\}$ is introduced.

Now, according to De Donder, the rate I_r of reaction r is defined as

$$I_r \equiv \frac{\mathrm{d}\xi_r}{\mathrm{d}t} = \frac{1}{\nu_{kr}} \frac{d_r n_k}{\mathrm{d}t}, \quad (r = 1, \dots, R) \tag{1.3}$$

where n_k is the mole number of component k, $d_r n_k$ is its change due to advancement of reaction r during time dt. The reaction rate is a measure of the speed of the reaction and plays the role of a generalized flux in the sense of the Onsager theory. The variable ξ_r is the degree of advancement or the extent of the reaction. Evidently the change of the mole number of component k due to advancement of all reactions is

$$\mathrm{d}n_k = \sum_{r=1}^{R} d_r n_k = \sum_{r=1}^{R} \nu_{kr} \mathrm{d}\xi_r, \quad (k = 1, \dots, K), \tag{1.4}$$

i.e., the relations between the component velocities and reaction rates are

$$I_k \equiv \frac{\mathrm{d}n_k}{\mathrm{d}t} = \sum_{r=1}^{R} \nu_{kr} I_r, \quad (k = 1, \dots, K) \tag{1.5}$$

which are important relations because only component velocities I_k are directly measurable quantities.

2. Basic equations of the thermodynamics of closed systems

The first law of thermodynamics for a closed system in case of a simple external force is

$$dU = dQ - pdV \tag{2.1}$$

where dU is the change of internal energy of the system, dQ is the heat transferred to the system, and $-pdV$ is the work performed on the system by external pressure. If no irreversible processes take place in the system, then

$$dU = TdS - pdV \tag{2.2}$$

where T is the absolute temperature of the system and dS is its reversible entropy change. If, however, irreversible processes take place in the system then

$$dU = TdS - pdV - Td_i S \tag{2.3}$$

where $d_iS \geq 0$ is the entropy change due to irreversible processes. Under the conditions S, $V =$ constant,

$$(dU)_{S,V} = -Td_iS \leq 0 \tag{2.4}$$

is the internal energy dissipation in the system due to the irreversible processes. Similarly, if we use the definition of the free energy F, enthalpy H and Gibbs' potential G, we have

$$dF = -SdT - pdV - Td_iS, \tag{2.5}$$

$$dH = TdS + Vdp - Td_iS, \tag{2.6}$$

$$dG = -SdT + Vdp - Td_iS. \tag{2.7}$$

Consequently, the expressions for various kinds of energy dissipation under given conditions of external constraint are:

$$(dF)_{T,V} = (dH)_{S,p} = (dG)_{T,p} = -Td_iS \leq 0 \tag{2.8}$$

In closed systems at constant temperature and pressure the free enthalpy $G = G(T, p, n_1, \ldots, n_K)$ is a function of the mole numbers only and consequently,

$$(\mathrm{d}G)_{T,p} = \sum_{k=1}^{K} \mu_k \, \mathrm{d}n_k, \quad \mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,p}, \quad (k = 1, \ldots, K) \tag{2.9}$$

where μ_k is the chemical potential of component k. Now, combining equations (1.4), (2.8) and (2.4), we obtain

$$d_i S = \begin{cases} -\dfrac{1}{T} \displaystyle\sum_{k=1}^{K} \mu_k \, \mathrm{d}n_k = \sum_{k=1}^{K} X_k \, \mathrm{d}n_k \\ -\dfrac{1}{T} \displaystyle\sum_{k=1}^{K} \sum_{r=1}^{R} \mu_k \nu_{kr} \, \mathrm{d}\xi_r = \dfrac{1}{T} \sum_{r=1}^{R} A_r \, \mathrm{d}\xi_r \end{cases} \tag{2.10}$$

where two equivalent representations of the irreversible entropy variation are introduced, by which two different but equivalent descriptions of the phenomena are possible with the forces

$$X_k \equiv -\frac{\mu_k}{T}, \ (k = 1, \ldots, K); \ A_r \equiv -\sum_{k=1}^{K} \nu_{kr} \mu_k, \ (r = 1, \ldots, R). \tag{2.11}$$

It is well known that the X_k forces belong to the so-called "component representation", while if we prefer to select affinities A_r as thermodynamic forces, "reaction representation" is used. In the forthcoming, "reaction representation" will be used, which is preferable for the analysis of principal questions. By definition,

$$\mathcal{P} \equiv \frac{d_iS}{\mathrm{d}t} = -\frac{1}{T} \left(\frac{\partial G}{\partial t}\right)_{p,T} = \sum_{k=1}^{K} I_k X_k = \frac{1}{T} \sum_{r=1}^{R} I_r A_r \geq 0 \tag{2.12}$$

is the entropy production per unit time in the total closed system being non-negative due to the second law.

Equation (2.12) is generally valid, irrespective of the linear or non-linear character of the constitutive equations between I_k and X_k, or I_r and A_r respectively.

Equation (2.12) can be used for calculations only if the constitutive (or material) equations (for selection in "reaction representation")

$$I_r = f_r(A_1, \dots, A_R); \quad (r = 1, \dots, R) \tag{2.13}$$

are known. In reaction kinetics they are called rate functions. They are homogeneous functions, i.e., they all vanish if all affinities vanish. In other words, there are no fluxes in the absence of forces.

In linear non-equilibrium thermodynamics linear constitutive equations

$$I_r = \sum_{s=1}^{R} L_{rs} A_s; \quad (r = 1, \dots, R) \tag{2.14}$$

are assumed together with Onsager reciprocal relations

$$L_{rs} = L_{sr}; \quad (r, s = 1, \dots, R) \tag{2.15}$$

The coefficients L_{rs} $(r, s = 1, \dots, R)$ are called chemical drag coefficients. In the case of R stoichiometrically independent reactions the number of Onsager relations is $R(R-1)/2$.

3. General forms of reaction rate functions

Let any of reactions (1.1) be a single reaction in the sense that its advancement can be described by a single parameter ξ_r. The reaction may be a single step if it proceeds at the molecular level as written. In this case the reaction rate function is of the form first suggested by GULDBERG and WAAGE, i.e., the rates of the reaction from the left to the right of equations (1.1) are

$$I'_r = k'_r \prod_{k'} \left(\frac{n_{k'}}{n}\right)^{\nu_{k'r}} \quad (r = 1, \dots, R), \tag{3.1}$$

while the rates in the reverse direction are

$$I''_r = k''_k \prod_{k''} \left(\frac{n_{k''}}{n}\right)^{\nu_{k''r}} \quad (r = 1, \dots, R) \tag{3.2}$$

where k'_r and k''_r denote forward and backward rate constants, respectively, and n is the sum of mole numbers of all components. The net reaction rates are

$$I_r = I'_r - I''_r = k'_r \prod_{k'} \left(\frac{n_{k'}}{n}\right)^{\nu_{k'r}} - k''_r \prod_{k''} \left(\frac{n_{k''}}{n}\right)^{\nu_{k''r}}. \tag{3.3}$$

In equilibrium, we assume the validity of the principle of detailed balance, according to which

$$I_r^e = 0, \text{ i.e. } I_r'^e = I_r''^e \quad (r = 1, \dots, R) \tag{3.4}$$

separately for all r-s. (Superscript e stands for equilibrium.) Hence,

$$k_r' \prod_{k'} \left(\frac{n_{k'}^e}{n}\right)^{\nu_{k'r}} = k_r'' \prod_{k''} \left(\frac{n_k^{e''}}{n}\right)^{\nu_{k''r}} = I_r^e \tag{3.5}$$

is the explicit form of the principle of detailed balance, consequently

$$\frac{k_r'}{k_r''} = \frac{\prod\limits_{k''} \left(\frac{n_{k''}^e}{n}\right)^{\nu_{k''r}}}{\prod\limits_{k'} \left(\frac{n_{k'}^e}{n}\right)^{\nu_{k'r}}} = K_r ; \quad (r = 1, \dots, R) \tag{3.6}$$

where K_r is the thermodynamic equilibrium constant if the system is an ideal one. Equations (3.4) and (3.5) express that at equilibrium in the sense of the principle of detailed balance, all elementary steps proceed at the same rate as their reverse.

4. Stoichiometrically dependent kinetic systems

A kinetic system is called stoichiometrically dependent if some of the reaction equations can be derived from others by means of linear combination. Evidently, if the stoichiometric matrix $\{\nu_{kr}\}$ $(k = 1, \dots, K;\ r = 1, \dots, R)$ has the rank $\varrho < R$, then only ϱ equations are linearly independent.

Let these ϱ independent reactions be represented by

$$\sum_{k=1}^{K} \nu_{kr'} M_k = 0 ; \quad (r' = 1, \dots, \varrho) \tag{4.1}$$

and the $R - \varrho$ dependent reactions by the equations

$$\sum_{k=1}^{K} \nu_{kr''} M_k = 0 ; \quad (r'' = \varrho + 1, \dots, R) \tag{4.2}$$

The equations of the dependent reactions can be derived from independent ones by their linear combinations as

$$\sum_{r'=1}^{\varrho} \beta_{r'r''} \sum_{k=1}^{K} \nu_{kr'} M_k = \sum_{k=1}^{K} \nu_{kr''} M_k ; \quad (r'' = \varrho + 1, \dots, R) \tag{4.3}$$

where $\beta_{r'r''} \gtreqless 0$ (usually integers) are the coefficients of linear combination. From equation (4.3) it follows that

$$\nu_{kr''} = \sum_{r'=1}^{\varrho} \beta_{r'r''} \nu_{kr'} ; \quad (r'' = \varrho + 1, \dots, R;\ k = 1, \dots, K) . \tag{4.4}$$

The affinities of the dependent reactions can be derived from those of the independent ones by the use of (2.11) and (4.4) as follows

$$A_{r''} = -\sum_{k=1}^{K} \nu_{kr''}\,\mu_k = -\sum_{k=1}^{K}\sum_{r'=1}^{\varrho} \beta_{r\cdot r''}\,\nu_{kr'}\,\mu_k = \sum_{r'=1}^{\varrho} \beta_{r'r''}\,A_{r'}\,; \quad (r'' = \varrho + 1, \dots, R) \tag{4.5}$$

Evidently, from (4.5) an important formula follows, namely

$$\mathcal{A}_{r''} = e^{\frac{A_{r''}}{RT}} = e^{\sum\limits_{r'=1}^{\varrho} \beta_{r'r''} \frac{A_{r'}}{RT}} = \prod_{r'=1}^{\varrho} \mathcal{A}_{r'}^{\beta_{r'r''}}\,; \quad (r'' = \varrho + 1, \dots, R)\,. \tag{4.6}$$

Here $A_{r'}$ $(r = 1, \dots, \varrho)$ are the independent affinities and $A_{r''}(r'' = \varrho + 1, \dots, R)$ the dependent ones and, similarly, the $\mathcal{A}_{r'}$ are the independent while the $\mathcal{A}_{r''}$-s are the dependent exponentials of the adequate set of affinities.

The relations between the dependent reaction rates and independent thermodynamic fluxes can be derived from the postulate of the invariance of entropy production. Indeed, from the relation

$$T\mathcal{S} = \sum_{r=1}^{R} I_r A_r = \sum_{r'=1}^{\varrho} I_{r'}^{*} A_{r'} \tag{4.7}$$

where the $I_{r'}^{*}$-s denote independent thermodynamic fluxes and $A_{r'}$-s are, as known, independent affinities. Combining equations (4.5) and (4.7), we obtain

$$\begin{aligned} T\mathcal{S} &= \sum_{r=1}^{R} I_r A_r = \sum_{r'=1}^{\varrho} I_{r'} A_{r'} + \sum_{r''=\varrho+1}^{R} I_{r''} A_{r''} = \sum_{r'=1}^{\varrho} I_{r'} A_{r'} + \\ &+ \sum_{r''=\varrho+1}^{R} I_{r''} \sum_{r'=1}^{\varrho} \beta_{r'r''} A_{r'} = \sum_{r'=1}^{\varrho} \left(I_{r'} + \sum_{r''=\varrho+1}^{R} \beta_{r'r''}\, I_{r''} \right) A_{r'} \end{aligned} \tag{4.8}$$

and, consequently,

$$I_{r'}^{*} = I_{r'} + \sum_{r''=\varrho+1}^{R} \beta_{r'r''} I_{r''}\,; \quad (r' = 1, \dots, \varrho) \tag{4.9}$$

are the transformations between independent thermodynamic fluxes and dependent reaction rates, correspondingly,

$$d\xi_{r'}^{*} = d\xi_{r'} + \sum_{r''=\varrho+1}^{R} \beta_{r'r''}\, d\xi_{r''}\,; \quad (r' = 1, \dots, \varrho) \tag{4.10}$$

are the adequate transformations between the reaction variables. It is very easy to express the variations of the dn_k-s in terms of the stoichiometrically independent reaction variables, since

$$\begin{aligned} \sum_{r'=1}^{\varrho} \nu_{kr'}\, d\xi_{r'}^{*} &= \sum_{r'=1}^{\varrho} \nu_{kr'}\, d\xi_{r'} + \sum_{r'=1}^{\varrho} \nu_{kr'} \sum_{r''=\varrho+1}^{R} \beta_{r'r''}\, d\xi_{''} = \sum_{r'=1}^{\varrho} \nu_{kr'}\, d\xi_{r'} + \\ &+ \sum_{r''=\varrho+1}^{R} \sum_{r'=1}^{\varrho} \beta_{r'r''}\, \nu_{kr'}\, d\xi_{r''} = \sum_{r'=1}^{\varrho} \nu_{kr'}\, d\xi_{r'} + \sum_{r''=\varrho+1}^{R} \nu_{kr''}\, d\xi_{r''} = \sum_{r=1}^{R} \nu_{kr}\, d\xi_r = dn_k\,. \end{aligned} \tag{4.11}$$

In this derivation equations (4.10), (4.4) and (1.4) have been involved and the result is

$$dn_k = \sum_{r'=1}^{\varrho} \nu_{kr'}\, d\xi_{r'} = \sum_{r=1}^{R} \nu_{kr}\, d\xi_r \quad (k = 1, \ldots, K). \tag{4.12}$$

Thus, the dn_k-s are, of course, invariant quantities with respect to the reduction of the stoichiometrically dependent reaction system to a stoichiometrically equivalent but independent set of reactions.

5. Nonlinear constitutive equations for independent systems

In this section we shall derive the non-linear phenomenological equations expressing the reaction rates $I_r (r = 1, \ldots, R)$ as functions of the affinities $A_1, \ldots, A_R$. For the sake of simplicity, the derivation is restricted to ideal systems where

$$\mu_k = \mu_k^* + RT \ln \frac{n_k}{n}\,; \quad (k = 1, \ldots, K). \tag{5.1}$$

In such systems the affinity of reaction r is

$$A_r = -\sum_{k=1}^{K} \nu_{kr}\, \mu_k = -\sum_{k=1}^{K} \nu_{kr}\, \mu_k^* - RT \ln \prod_{k=1}^{K} \left(\frac{n_k}{n}\right)^{\nu_{kr}}. \tag{5.2}$$

Since in equilibrium $A_r = 0$, the first term on the right can be expressed as

$$-\sum_{k=1}^{K} \nu_{kr}\, \mu_k^* = RT \ln \prod_{k''} \left(\frac{n_{k''}^e}{n}\right)^{\nu_{k''r}} - RT \ln \prod_{k'} \left(\frac{n_{k'}^e}{n}\right)^{\nu_{k'r}} \tag{5.3}$$

where superscript e refers to equilibrium.

The second term on the right-hand side of equation (5.2) can be, in general, similarly separated into terms for reactants and products; and for the affinity we obtain

$$A_r = RT \ln \prod_{k'} \left(\frac{n_{k'}}{n_{k'}^e}\right)^{\nu_{k'r}} - RT \ln \prod_{k''} \left(\frac{n_{k''}}{n_{k''}^e}\right)^{\nu_{k''r}}. \tag{5.4}$$

The instantaneous state of the system at constant pressure and temperature can be characterized by the values

$$\Delta n_k = n_k - n_k^e; \quad (k = 1, \ldots, K) \tag{5.5}$$

in component representation, while in reaction representation by the deviations $\Delta\xi_1, \ldots, \Delta\xi_R$ from equilibrium by

$$\Delta n_k = \sum_{r=1}^{R} \nu_{kr}\, \Delta\xi_r, \quad (k = 1, \ldots, K). \tag{5.6}$$

Substituting equations (5.5) and (5.4)

$$\frac{A_r}{RT} = \ln \prod_{k'} \left(1 + \frac{\Delta n_{k'}}{n^e_{k'}}\right)^{\nu_{k'r}} - \ln \prod_{k''} \left(1 + \frac{\Delta n_{k''}}{n^e_{k''}}\right)^{\nu_{k''r}}, \tag{5.7}$$

i.e.,

$$\mathcal{A}_r(\Delta n_1, \ldots, \Delta n_k) = \frac{\prod_{k'} \left(1 + \frac{\Delta n_{k'}}{n^e_{k'}}\right)^{\nu_{k'r}}}{\prod_{k''} \left(1 + \frac{\Delta n_{k''}}{n^e_{k''}}\right)^{\nu_{k''r}}}, \quad (r = 1, \ldots, R). \tag{5.8}$$

Here, as well as already in equation (4.6) the new quantities

$$\mathcal{A}_r = e^{\frac{A_r}{RT}}; \quad (r = 1, \ldots, R) \tag{5.9}$$

have been introduced and expressed in component representation, which can appropriately be called as "absolute affinities", since these are closely related ($\mathcal{A}_r = \prod_{k=1}^{k} \lambda_k^{\nu_{kr}}$) to the "absolute activities" $\lambda_k = e^{\frac{\mu_k}{RT}}$ defined and widely used by GUGGENHEIM [45].

Substitution of relations (5.6) into equations (5.8) can express the "absolute affinities" in reaction representation as

$$\mathcal{A}_r(\Delta\xi_1, \ldots, \Delta\xi_R) = \frac{\prod_{k'} \left(1 + \frac{\sum_{r=1}^{R} \nu_{k'r} \Delta\xi_r}{n^e_{k'}}\right)^{\nu_{k'r}}}{\prod_{k''} \left(1 + \frac{\sum_{r=1}^{R} \nu_{k''r} \Delta\xi_r}{n^e_{k''}}\right)^{\nu_{k''r}}}; \quad (r = 1, \ldots, R). \tag{5.10}$$

This is a system of R algebraic equations in which the R values $\Delta\xi_1, \ldots, \Delta\xi_R$ may be considered as unknowns. In principle, this set of equations can be solved for $\Delta\xi_1, \ldots, \Delta\xi_R$ and the solution results the functions

$$\Delta\xi_r = f_r(\mathcal{A}_1, \ldots, \mathcal{A}_R) \text{ or } \Delta\xi_r = \varphi_r(A_1, \ldots, A_R); \ (r = 1, \ldots, R). \tag{5.11}$$

It should be noted that in the system (5.8) the number of unknown Δn-s is, at least in general, higher than the number of equations. Thus, the set of equations (5.8) cannot be unambiguously solved, i.e., the component representation is, in general, not useful for our purposes.

For systems where the Guldberg—Waage form (3.3) of the rate function holds, it is easy to transform the rate functions in which the reaction rates are functions of mole fractions $\frac{n_1}{n}, \ldots, \frac{n_k}{n}$ into relations where the reaction rates are functions of the reaction variables $\Delta\xi_1, \ldots, \Delta\xi_R$. Indeed, equation

(3.3) is equivalent to

$$I_r = k'_r \prod_{K'} \left(\frac{n^e_{K'}}{n}\right)^{\nu_{k'r}} \prod_{K'} \left(\frac{n_{K'}}{n^e_{K'}}\right)^{\nu_{k'r}} - k''_r \prod_{K''} \left(\frac{n^e_{K''}}{n}\right)^{\nu_{k''r}} \prod_{K''} \left(\frac{n_{K''}}{n^e_{K''}}\right)^{\nu_{k''r}}. \qquad (5.12)$$

Considering the principle of detailed balance (3.5) and relations (5.5), we obtain the reaction rates in component representation as

$$I_r = I^e_r \left[\prod_{K'} \left(1 + \frac{\Delta n_{K'}}{n^e_{K'}}\right)^{\nu_{k'r}} - \prod_{K''} \left(1 + \frac{\Delta n_{K''}}{n^e_{K''}}\right)^{\nu_{k''r}} \right]; \quad (r = 1, \ldots, R) \qquad (5.13)$$

or, by using (5.6) in reaction representation as:

$$I_r = I^e_r \left[\prod_{K'} \left(1 + \frac{\sum\limits_{r=1}^{R} \nu_{K'r} \Delta\xi_r}{n^e_{K'}}\right)^{\nu_{k'r}} - \prod_{K''} \left(1 + \frac{\sum\limits_{r=1}^{R} \nu_{K''r} \Delta\xi_r}{n^e_{K''}}\right)^{\nu_{k''r}} \right]; \quad (r = 1, \ldots, R). \qquad (5.14)$$

Finally, if the functions (5.11) are substituted for $\Delta\xi_r$ $(r = 1, \ldots, R)$ into the last equation, the desired non-linear phenomenological equations are arrived at

$$I_r = I^e_r \varphi_r(A_1, \ldots, A_R); \quad (r = 1, \ldots, R). \qquad (5.15)$$

Of course the practical success of this procedure depends on the possibility of solving equation system (5.10). For kinetically first order reactions this is a set of linear algebraic equations and the solution is very easily obtained. Also a system of quadratic algebraic equations (kinetically second order reactions) can be easily solved. However, a quadratic algebraic equation has two roots and the solution having a physical meaning must be chosen. As condition for this selection, vanishing of all $\Delta\xi$-s at equilibrium can be used. Of course, the solution of equations (5.10) for third or higher order reactions involves some difficulties. But such reactions (elementary steps) are very seldom, therefore such equations are of not much importance.

Let us compare equations (5.10) and (5.14). The functions of the forward and backward reaction rates

$$u'_r = \prod_{K'} \left(1 + \frac{\sum\limits_{r=1}^{R} \nu_{K'r} \Delta\xi_r}{n^e_{K'}}\right)^{\nu_{k'r}}; \quad u''_r = \prod_{K''} \left(1 + \frac{\sum\limits_{r=1}^{R} \nu_{K''r} \Delta\xi_r}{n^e_{K''}}\right)^{\nu_{k''r}} \qquad (5.16)$$

occur in both equations. Now, substituting equations (5.11) into (5.16) it can be seen that both u'_r and u''_r are functions of the affinities, i.e.,

$$u'_r = u'_r(A_1, \ldots, A_R); \quad u''_r = u''_r(A_1, \ldots, A_R). \qquad (5.17)$$

Consequently, equations (5.10) and (5.14) may be transformed into the forms

$$\mathcal{K}_r = \frac{u'_r(A_1, \ldots, A_R)}{u''_r(A_1, \ldots, A_R)} = \frac{u'_r}{u''_r} \qquad (5.18)$$

and

$$I_r = I_r^e\,[u_r'(A_1, \dots, A_R) - u_r''(A_1, \dots, A_R)] = I_r^e(u_r' - u_r''), \qquad (5.19)$$

respectively. Combining (5.18) and (5.19), we obtain general non-linear constitutive equations between reaction rates and affinities in the form:

$$I_r = I_r^e(\mathcal{A}_r - 1)\, u_r''(A_1, \dots, A_R); \quad (r = 1, \dots, R). \qquad (5.20)$$

In these equations the rate function of reaction r is separated into three factors (1) I_r^0 — which depends only on temperature, pressure and, on the equilibrium compositions (see Eqs. (3.5)) but does not depend on the affinities; (2) the second factor $\mathcal{A}_r - 1 = e^{\frac{A_r}{RT}} - 1$ which depends only on one absolute affinity or affinity, respectively (that of the same reaction); (3) the third factor u_r'' which depends on all affinities.

6. On the existence of Onsager's relation

a) *Stoichiometrically independent systems*

In stoichiometrically independent kinetic systems equations (1.1) are linearly independent, i.e., none of them can be derived by linear combination of the others. Consequently, the variables $A_r (r = 1, \dots, R)$ and $\Delta\xi_r (r = 1, \dots, R)$ are also linearly independent.

Rate functions (5.15) or (5.20) can be expanded in Taylor's series around equilibrium, and, if only first order terms are considered

$$I_r = \sum_{s=1}^{R} L_{rs} A_s; \quad (r = 1, \dots, R), \qquad (6.1)$$

since reaction rates vanish in equilibrium. The coefficients L_{rs} are related to the equilibrium values of the partial derivatives by means of

$$L_{rs} = \left(\frac{\partial I_r}{\partial A_s}\right)_e \quad (r, s = 1, \dots, R) \qquad (6.2)$$

where subscript e refers to equilibrium.

The Onsager reciprocal relations express that $L_{rs} = L_{sr} (r, s = 1, \dots, R)$ or alternatively,

$$\left(\frac{\partial I_r}{\partial A_s}\right)_e = \left(\frac{\partial I_s}{\partial A_r}\right)_e; \quad (r, s = 1, \dots, R). \qquad (6.3)$$

In this section these relations will prove to be trivially satisfied in a stoichiometrically independent system where the alternative form (5.20) of the Guldberg—Waage rate function holds.

The proof starts with equation (5.20). Its partial derivation with respect to A_s yields

$$\frac{\partial I_r}{\partial A_s} = \frac{d\mathcal{A}_s}{dA_s} I_r^0 \left[\delta_{rs} u_r'' + (\mathcal{A}_r - 1) \frac{\partial u_r''}{\partial \mathcal{A}_s} \right] \tag{6.4}$$

where δ_{rs} denotes the Kronecker symbol. In equilibrium we have

$$u_r'' = 1 \quad \text{and} \quad \mathcal{A}_r = 1 \tag{6.5}$$

together with

$$\left(\frac{d\mathcal{A}_s}{dA_s} \right)_e = \left(\frac{\exp \frac{\mathcal{A}_s}{RT}}{RT} \right)_e = \frac{1}{RT}. \tag{6.6}$$

Therefore, the final result is

$$\left(\frac{\partial I_r}{\partial A_s} \right)_e = \frac{I_r^e}{RT} \delta_{rs}; \quad (r, s = 1, \ldots, R). \tag{6.7}$$

Thus, the following theorem can be stated.

Theorem I: *For every stoichiometrically independent network of chemical reactions in the linear domain of constitutive equations, the Onsager reciprocity relations are satisfied in a trivial manner, i.e.*

$$\left(\frac{\partial I_r}{\partial A_s} \right)_e = \left(\frac{\partial I_s}{\partial A_r} \right)_e = 0. \tag{6.8}$$

In other words, in the linear approximation the matrix of the chemical conductivity coefficients

$$L_{rs} = \frac{1}{RT} \begin{pmatrix} I_1^e & 0 & 0 & \ldots & 0 \\ 0 & I_2^e & 0 & \ldots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \ldots & I_R^e \end{pmatrix} \tag{6.9}$$

is diagonal.

b) *Stoichiometrically dependent systems*

Let us consider now stoichiometrically dependent reaction systems. In such systems the stoichiometrically independent and dependent reactions are defined by equations (4.1) and (4.2), respectively. It is seen from equation (4.12) that

$$\Delta n_k = \sum_{r=1}^{R} \nu_{kr} \Delta \xi_r = \sum_{r'=1}^{\varrho} \nu_{kr'} \Delta \xi_{r'}^*; \quad (k = 1, \ldots, K); \tag{6.10}$$

here Δn_k, $\Delta \xi_r$ and $\Delta \xi_{r'}^*$ are the deviations from equilibrium in component representation, reaction representation and stoichiometrically equivalent independent reaction representation, respectively.

Substituting these relations into the first ϱ equations (5.8), the independent set of absolute affinities are obtained as:

$$\mathcal{A}_{r'}(\Delta\xi_1^*, \ldots, \Delta\xi_\varrho^*) = \frac{\prod\limits_{k'}\left(1 + \frac{\sum\limits_{r'=1}^{\varrho} \nu_{k'r'}\,\Delta\xi_{r'}^*}{n_{k'}^e}\right)^{\nu_{k'r'}}}{\prod\limits_{k''}\left(1 + \frac{\sum\limits_{r'=1}^{\varrho} \nu_{k''r'}\,\Delta\xi_{r'}^*}{n_{k''}^e}\right)^{\nu_{k''r'}}}\,; \quad (r' = 1, \ldots, \varrho); \quad (6.11)$$

i.e., the absolute affinities are expressed now in terms of the stoichiometrically equivalent independent set of $\Delta\xi_1^*, \ldots, \Delta\xi_\varrho^*$. This set of expressions contain ϱ equations for the ϱ unknowns: $\Delta\xi_1^*, \ldots, \Delta\xi_\varrho^*$ of the independent reactions.

Solution of system (6.11) of algebraic equations results in functions

$$\Delta\xi_{r'}^* = f_{r'}^*(\mathcal{A}_1, \ldots, \mathcal{A}_\varrho); \quad (r' = 1, \ldots, \varrho) \qquad (6.12)$$

and after substitution of the first ϱ equations (5.9), the equations

$$\Delta\xi_{r'}^* = F_{r'}^*(A_1, \ldots, A_\varrho); \quad (r' = 1, \ldots, \varrho) \qquad (6.13)$$

are obtained. Now, substituting equation (6.10) into the second equation (5.16), we obtain the u_r''-s $(r = 1, \ldots, R)$ as functions of the independent variables $\Delta\xi_r^*$, $(r = 1, \ldots, \varrho)$ only. Furtheron, substituting equations (6.13) into these functions, it can be seen that the u_r''-s are functions only of the independent affinities, i.e.,

$$u_r'' = u_r''(A_1, \ldots, A_\varrho)\,; \quad (r = 1, \ldots, R). \qquad (6.14)$$

Evidently, the number of these u_r''-s is R.

In consequence of equations (5.20) and (6.14) the constitutive equations are gained

$$I_r = I_r^e\left(e^{\frac{A_e}{RT}} - 1\right)u_r''(A_1, \ldots, A_\varrho)\,; \quad (r = 1, \ldots, R) \qquad (6.15)$$

which are analogues to equations (5.20) with the difference that in (6.15) the functions u_r'' do not depend on the eliminated dependent affinities $A_{\varrho+1}, \ldots, \ldots, A_R$.

Combining equations (4.9) and (6.15) we obtain for the independent fluxes

$$I_{r'}^* = I_{r'}^e\left(e^{\frac{A_{r'}}{RT}} - 1\right)u_{r'}'' + \sum_{r''=\varrho+1}^{R} \beta_{r'r''}\, I_{r''}^e\left(e^{\frac{A_{r''}}{RT}} - 1\right)u_{r''}''; \quad (r' = 1, \ldots, \varrho). \quad (6.16)$$

Considering the relations (4.6), the following expressions

$$I_{r'}^* = I_{r'}^e\left(e^{\frac{A_{r'}}{RT}} - 1\right)u_{r'}'' + \sum_{r''=\varrho+1}^{R} \beta_{r'r''}\, I_{r''}^e\left(e^{\sum\limits_{r'=1}^{\varrho} \beta_{r'r''}\frac{A_{r''}}{RT}} - 1\right)u_{r''}''; \quad (r' = 1, \ldots, \varrho) \quad (6.17)$$

are obtained for the independent fluxes. Now, partial differentiation with respect to A_s leads to

$$\frac{\partial I^*_{r'}}{\partial A_s} = \frac{\exp\left(\frac{A_s}{RT}\right)}{RT}\left\{I^e_{r'}\left[\delta_{r's}\, u''_{r'} + (\mathcal{A}_{r'}-1)\frac{\partial u''_{r'}}{\partial \mathcal{A}_s}\right] + \sum_{r''=\varrho+1}^{R}\frac{\beta_{r'r''}\beta_{sr''}}{\mathcal{A}_s} I^e_{r''}\prod_{r'=1}^{\varrho}\mathcal{A}_{r'}^{\beta_{r'r''}}\, u''_{r''} + \right.$$
$$\left. + \sum_{r''=\varrho+1}^{R}\beta_{r'r''} I^e_{r''}\left(\prod_{r'=1}^{\varrho}\mathcal{A}_{r'}^{\beta_{r'r''}} - 1\right)\frac{\partial u''_{r''}}{\partial \mathcal{A}_s}\right\}; \quad (r' = 1, \ldots, \varrho). \tag{6.18}$$

Since we have the following equilibrium values

$$(u''_{r'})_e = (u''_{r''})_e = (\mathcal{A}_{r'})_e = \left(\prod_{r'=1}^{\varrho}\mathcal{A}_{r'}^{\beta_{r'r''}}\right)_e = \left(\exp\left(\frac{A_s}{RT}\right)\right)_e = 1 \tag{6.19}$$

for all r' and r'', consequently, in equilibrium

$$\left(\frac{\partial I^*_{r'}}{\partial A_s}\right)_e = \frac{1}{RT}\left(\delta_{r's} I^e_{r'} + \sum_{r''=\varrho+1}^{R}\beta_{r'r''}\beta_{sr''} I^e_{r''}\right); \quad (r', s = 1, \ldots, \varrho). \tag{6.20}$$

Clearly, the second term on the right is symmetric with respect to r and s and, therefore, the final results

$$\left(\frac{\partial I^*_{r'}}{\partial A_s}\right)_e = \left(\frac{\partial I^*_s}{\partial A_{r'}}\right)_e \neq 0; \quad (r', s = 1, \ldots, \varrho) \tag{6.21}$$

are attained. Now, the following theorem can be stated.

Theorem II: *In every stoichiometrically dependent network of chemical reactions for the stoichiometrically equivalent independent set of linear constitutive equations the Onsager reciprocity relations are satisfied in a real fashion.*

Indeed, in the linear approximation, from (6.20) it can be concluded that the matrix of the chemical conductivity coefficients

$$L_{rs} = \begin{pmatrix} I^e_1 + \Sigma\beta_{1r''} I^e_{r''} & \Sigma\beta_{1r''}\beta_{2r''} I^e_{r''} & \ldots & \Sigma\beta_{1r''}\beta_{\varrho r''} I^e_{r''} \\ \Sigma\beta_{2r''}\beta_{1r''} I^e_{r''} & I^e_2 + \Sigma\beta^2_{2r''} I^e_{r''} & \ldots & \Sigma\beta_{2r''}\beta_{\varrho r''} I^e_{r''} \\ \vdots & \vdots & & \vdots \\ \Sigma\beta_{\varrho r''}\beta_{1r''} I^e_{r''} & \Sigma\beta_{\varrho r''}\beta_{2r''} I^e_{r''} & & I^e_\varrho + \Sigma\beta^2_{\varrho r''} I^e_{r''} \end{pmatrix} \tag{6.22}$$

is a symmetric one.

In Theorem I and II it is summarized that the Onsager reciprocity relations are satisfied in case of both independent and dependent chemical kinetic systems, provided that all reactions are elementary reversible reactions. In independent systems the Onsager reciprocity relations are satisfied trivially, whereas, in dependent systems for the stoichiometrically equivalent independent set of linear constitutive equations in a non-trivial fashion.

7. Examples

a) *The kinetic system* $M_1 \rightleftharpoons M_2$; $M_3 \rightleftharpoons M_4$

In this kinetic system there are two first order reactions:

$$-M_1 + M_2 = 0, \qquad -M_3 + M_4 = 0. \tag{7.1}$$

The components participating in the first reaction are inactive in the second and, of course, vice versa. Correspondingly, the stoichiometric matrix

$$\nu_{kr} = \begin{pmatrix} -1 & 0 \\ 1 & 0 \\ 0 & -1 \\ 0 & 1 \end{pmatrix} \tag{7.2}$$

has the rank 2: the two reactions are stoichiometrically independent, even separated since any row of the matrix has only one single non zero element. There are two equations of the type (5.8) and (5.10) each

$$e^{\frac{A_1}{RT}} = \mathcal{A}_1 = \frac{1 + \dfrac{\Delta n_1}{n_1^e}}{1 + \dfrac{\Delta n_2}{n_2^e}}; \qquad e^{\frac{A_2}{RT}} = \mathcal{A}_2 = \frac{1 + \dfrac{\Delta n_3}{n_3^e}}{1 + \dfrac{\Delta n_4}{n_4^e}} \tag{7.3}$$

and

$$\mathcal{A}_1 = \frac{1 - \dfrac{\Delta \xi_1}{n_1^e}}{1 + \dfrac{\Delta \xi_1}{n_2^e}}; \qquad \mathcal{A}_2 = \frac{1 - \dfrac{\Delta \xi_2}{n_3^e}}{1 + \dfrac{\Delta \xi_2}{n_4^e}}. \tag{7.4}$$

The last two equations have the solution

$$\Delta \xi_1 = n_1^e n_2^e \frac{1 - e^{\frac{A_1}{RT}}}{n_2^e + n_1^e e^{\frac{A_1}{RT}}}; \qquad \Delta \xi_2 = n_3^e n_4^e \frac{1 - e^{\frac{A_2}{RT}}}{n_4^e + n_3^e e^{\frac{A_2}{RT}}} \tag{7.5}$$

which vanish in equilibrium, where $A_1 = A_2 = 0$.

Substituting these into the rate equations of type (5.14), we obtain the exact nonlinear equations in the form

$$I_1 = I_1^e \left[1 - \frac{\Delta \xi_1}{n_1^e} - \left(1 + \frac{\Delta \xi_1}{n_2^e} \right) \right] = -(n_1^e + n_2^e) \frac{1 - e^{\frac{A_1}{RT}}}{n_2^e + n_1^e e^{\frac{A_1}{RT}}} \tag{7.6}$$

$$I_2 = I_2^e \left[1 - \frac{\Delta \xi_2}{n_3^e} - \left(1 + \frac{\Delta \xi_2}{n_4^e} \right) \right] = -(n_3^e + n_4^e) \frac{1 - e^{\frac{A_2}{RT}}}{n_4^e + n_3^e e^{\frac{A_2}{RT}}}. \tag{7.7}$$

The coefficients of the Onsagerian type linear theory can be obtained as equilibrium values of the first partial derivatives with respect to A_1 and A_2. These are

$$L_{11} = \left(\frac{\partial I_1}{\partial A_1}\right)_e = \frac{I_1^e}{RT}; \quad L_{22} = \left(\frac{\partial I_2}{\partial A_2}\right) = \frac{I_2^e}{RT} \tag{7.8}$$

and

$$L_{12} = \left(\frac{\partial I_1}{\partial A_2}\right)_e = 0 = \left(\frac{\partial I_2}{\partial A_1}\right)_e = L_{21}.$$

From this it can be seen that the Onsager reciprocal relations are trivially satisfied in accordance to Theorem I.

In this particular case Rysselberghe's, generalized reciprocal relations

$$\frac{\partial I_1}{\partial A_2} = \frac{\partial I_2}{\partial A_1} = 0 \tag{7.9}$$

are also trivially satisfied, since I_1 does not depend on A_2 and I_2 does not depend on A_1. Corresponding to equations (7.9) all higher order cross coefficients are zero, for instance: $L_{112} = L_{211} = L_{212} = L_{122} = 0$, since the higher partial derivatives of one reaction rate with respect to the affinity of the other reaction all vanish in equilibrium. Of course, this is an a priori trivial consequence of the stoichiometrically separated character of the reaction system (7.1)

b) *The consecutive reactions* $M_1 \rightleftharpoons M_2 \rightleftharpoons M_3$

In this system there are also two reactions but in contrast to the previous system, it contains one component which partakes in both reactions. The stoichiometric matrix

$$\nu_{kr} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix} \tag{7.10}$$

is of rank two. Therefore, the two reactions are stoichiometrically independent and equations (5.6) read in this case as

$$\Delta n_1 = -\Delta\xi_1; \quad \Delta n_2 = \Delta\xi_1 - \Delta\xi_2; \quad \Delta n_3 = \Delta\xi_2; \tag{7.11}$$

thus, equations (5.10) after rearrangement read as

$$\begin{aligned} -\left(\frac{1}{n_1^e} + \frac{\mathcal{A}_1}{n_2^e}\right)\Delta\xi_1 + \frac{\mathcal{A}_1}{n_2^e}\Delta\xi_2 &= \mathcal{A}_1 - 1 \\ \frac{1}{n_2^e}\,\Delta\xi_1 - \left(\frac{1}{n_2^e} + \frac{\mathcal{A}_2}{n_3^e}\right)\Delta\xi_2 &= \mathcal{A}_2 - 1. \end{aligned} \tag{7.12}$$

Their solution is

$$\begin{aligned} \Delta\xi_1 &= n_1^e \frac{n_3^e + n_2^e \mathcal{A}_2 - (n_2^e + n_3^e)\mathcal{A}_1 \mathcal{A}_2}{n_3^e + n_2^e \mathcal{A}_2 + n_1^e \mathcal{A}_1 \mathcal{A}_2} \\ \Delta\xi_2 &= n_3^e \frac{n_1^e + n_2^e - n_2^e \mathcal{A}_2 - n_1^e \mathcal{A}_1 \mathcal{A}_2}{n_3^e + n_2^e \mathcal{A}_2 + n_1^e \mathcal{A}_1 \mathcal{A}_2} . \end{aligned} \tag{7.13}$$

Substituting this into the rate functions of type (5.14) we obtain the nonlinear phenomenological equations as

$$\begin{aligned} I_1 &= I_1^e n \frac{\left(e^{\frac{A_1}{RT}} - 1\right) e^{\frac{A_2}{RT}}}{n_3^e + n_2^e e^{\frac{A_2}{RT}} + n_1^e e^{\frac{A_1+A_2}{RT}}} \\ I_2 &= I_2^e n \frac{e^{\frac{A_2}{RT}} - 1}{n_3^e + n_1^e e^{\frac{A_2}{RT}} + n_1^e e^{\frac{A_1+A_2}{RT}}} \end{aligned} \tag{7.14}$$

where n is the sum of the equilibrium mole numbers of components 1, 2 and 3.

In this system, in contrast to the previous example, both reaction rates depend on both affinities. In this sense the reactions are kinetically coupled.

If the equilibrium values of the partial derivatives of the rate functions (7.14) are calculated, then

$$L_{12} = L_{21} = 0, \tag{7.15}$$

i.e., the Onsager reciprocal relations are also trivially satisfied. This result is, however, not an a priori trivial one, but is in full agreement with our first general theorem, since consecutive reactions exhibit a very typical form of the stoichiometrically independent network of reactions. We can express the physical content of (7.15) as follows: in the linear domain of constitutive equations of chemical kinetics if the reaction system represents a stoichiometrically independent network of the given mechanism, there is no Onsager coupling between the independent reactions.

However, it is very easy to show that in the case of higher order approximation the kinetically uncoupled character of a stoichiometrically independent (but not separated !) reaction network is destroyed, at least in the Rysselberghe theory, when the validity of the following approximation is accepted:

$$I_r = \sum_s L_{rs} A_s + \frac{1}{2} \sum_{s,t} L_{rst} A_s A_t + \frac{1}{6} \sum_{s,t,v} L_{rstv} A_s A_t A_v + \ldots \qquad (r, s, t, v = 1, 2, \ldots) \tag{7.16}$$

Indeed, by calculating the values

$$L_{rst} = \left(\frac{\partial^2 I_r}{\partial A_s \partial A_t}\right)_e \quad \text{and} \quad L_{rstv} = \left(\frac{\partial^3 I_r}{\partial A_s \partial A_t \partial A_v}\right)_e \tag{7.17}$$

we have for the higher order coefficients,

$$L_{111} = \frac{I_1^e}{(RT)^2}(1 - 2x_1^e); \quad L_{112} = L_{121} = \frac{I_1^e}{n(RT)^2} x_3^e; \quad L_{122} = 0$$

$$L_{211} = 0; \quad L_{212} = L_{221} = -\frac{I_2^e}{n(RT)^2} x_1^e; \quad L_{222} = \frac{I_2^e}{(RT)^2}(2x_3^e - 1)$$

$$L_{1111} = \frac{I_1^e}{(RT)^3}(1 - 6x_1^e + 6x_1^{e2}); \quad L_{1112} = \frac{I_1^e}{(RT)^3}(-3x_1^e + x_2^e + x_3^e)$$

$$L_{1122} = \frac{I_2^e}{(RT)^3} x_3^e(-x_1^e - x_2^e + x_3^e); \quad L_{1222} = L_{2111} = 0$$

$$L_{2112} = \frac{I_2^e}{(RT)^3} x_1^e(x_1^e - x_2^e - x_3^e); \quad L_{2122} = \frac{I_2^e}{(RT)^3} x_1^e(x_1^e + x_2^e - 3x_3^e)$$

$$L_{2222} = \frac{I_2^e}{(RT)^3}(1 - 6x_1^e x_3^e - 6x_2^e x_3^e)$$

(where x_k^e is the equilibrium mole fraction). It can be seen that in higher order approximations the RGRR-s are not satisfied. In other words, consecutive reactions exhibit a stoichiometrically independent but not separated network of elementary steps. Consequently, this set of reactions in linear approximation is considered only as a kinetically uncoupled one, due to the trivial validity of Onsager's relation. However, in higher order approximations they are governed by kinetically coupled constitutive equations but for higher order coupling coefficients the RGRR-s are no longer valid.

c) *The kinetic system* $2M_1 \rightleftharpoons M_2 \rightleftharpoons M_3$

For illustration of our general method to obtain exact and explicit expressions for nonlinear reaction rate-affinity type constitutive equations, let us consider a somewhat more complicated type of reaction. In this example

$$-2M_1 + M_2 = 0, \quad -M_2 + M_3 = 0 \tag{7.18}$$

the first reaction is of second order and the second reaction is of first order. The stoichiometric matrix

$$\nu_{kr} = \begin{pmatrix} -2 & 0 \\ 1 & -1 \\ 0 & 1 \end{pmatrix} \tag{7.19}$$

is of rank two. Thus, in the system we have also two stoichiometrically independent reactions. The deviation from equilibrium is characterized by

$$\Delta n_1 = -2\Delta\xi_1; \; \Delta n_2 = \Delta\xi_1 - \Delta\xi_2; \; \Delta n_3 = \Delta\xi_2. \tag{7.20}$$

The (5.10) type equations are the following

$$\mathcal{A}_1 = \frac{\left(1 - \dfrac{2\Delta\xi_1}{n_1^e}\right)^2}{1 + \dfrac{\Delta\xi_1}{n_2^e} - \dfrac{\Delta\xi_2}{n_2^e}}\,; \qquad \mathcal{A}_2 = \frac{1 + \dfrac{\Delta\xi_1}{n_2^e} - \dfrac{\Delta\xi_2}{n_2^e}}{1 + \dfrac{\Delta\xi_2}{n_3^e}} \tag{7.21}$$

which have the solutions

$$\Delta\xi_1 = \frac{n_1^e}{8R(\mathcal{A}_2)}\left[P_1(\mathcal{A}_1, \mathcal{A}_2) - Q(\mathcal{A}_1, \mathcal{A}_2)\right] \tag{7.22}$$

$$\Delta\xi_2 = \frac{n_3^e}{8R(\mathcal{A}_2)}\left[\frac{P_2(\mathcal{A}_1, \mathcal{A}_2)}{R(\mathcal{A}_2)} - \frac{n_1^e Q(\mathcal{A}_1, \mathcal{A}_2)}{R(\mathcal{A}_2)}\right] \tag{7.23}$$

where

$$\begin{aligned}
P_1(\mathcal{A}_1, \mathcal{A}_2) &= 4n_3^e + 4n_2^e\mathcal{A}_2 + n_e^1\mathcal{A}_1\mathcal{A}_2 \\
P_2(\mathcal{A}_1, \mathcal{A}_2) &= 4n_3^e(n_1^e + 2n_2^e) + 4n_2^e(n_1^e + 2n_2^e - 2n_3^e)\mathcal{A}_2 - 8n_2^e\mathcal{A}_2^2 + (n_1^e)^2\mathcal{A}_1\mathcal{A}_2 \\
Q(\mathcal{A}_1, \mathcal{A}_2) &= \sqrt{\mathcal{A}_1\mathcal{A}_2[8(n_1^e + 2n_2^e + 2n_3^e)(n_3^e + n_2^e\mathcal{A}_2) + (n_1^e)^2\mathcal{A}_1\mathcal{A}_2]} \\
R(\mathcal{A}_2) &= n_3^e + n_2^e\mathcal{A}_2.
\end{aligned} \tag{7.24}$$

Notice, that the quadratic equation (7.21) has two solutions but one of these can be excluded because it does not vanish in equilibrium. Now, the rate functions read as

$$I_1 = I_1^e\left[\left(1 - \frac{2\Delta\xi_1}{n_1^e}\right)^2 - \left(1 + \frac{\Delta\xi_1}{n_2^e} - \frac{\Delta\xi_2}{n_2^e}\right)\right] \tag{7.25}$$

$$I_2 = I_2^e\left[1 + \frac{\Delta\xi_1}{n_2^e} - \frac{\Delta\xi_2}{n_2^e} - \left(1 + \frac{\Delta\xi_2}{n_3^e}\right)\right], \tag{7.26}$$

or with the use of (7.21)

$$I_1 = I_1^e(\mathcal{A}_1 - 1)\left(1 + \frac{\Delta\xi_1}{n_2^e} - \frac{\Delta\xi_2}{n_2^e}\right) \tag{7.27}$$

$$I_2 = I_2^e(\mathcal{A}_2 - 1)\left(1 + \frac{\Delta\xi_2}{n_3^e}\right). \tag{7.28}$$

Substituting (7.22) and (7.23) we obtain the exact nonlinear constitutive equations expressed in terms of absolute affinities, i.e.,

$$I_1 = I_1^e(\mathcal{A}_1 - 1)\frac{P_3 - n_1^e\mathcal{A}_2 Q}{8R^2} \tag{7.29}$$

$$I_2 = I_2^e(\mathcal{A}_2 - 1)\left\{1 + \frac{1}{8R^2}(P_2 - n_1^e Q)\right\} \tag{7.30}$$

where

$$P_3(\mathcal{A}_1, \mathcal{A}_2) = 4\,[n_1^e n_2^e + n_1^e n_e^3 + 2n_2^e n_3^e + 2(n_3^e)^2]\,\mathcal{A}_2 + \\ + 8n_2^e(n_2^e + n_3^e)\,\mathcal{A}_2^2 + (n_1^e)^2\mathcal{A}_1\,\mathcal{A}_2^2$$

and

$$\mathcal{A}_1 = e^{\frac{A_1}{RT}}; \quad \mathcal{A}_2 = e^{\frac{A_2}{RT}}.$$

By the partial differentiation of equation (7.29) with respect to A_2 and (7.30) with respect to A_1, and taking the equilibrium values of the derivatives, it is seen that the Onsager relations are trivially satisfied, since in equilibrium

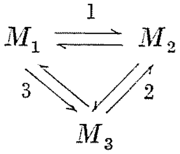
$$(\mathcal{A}_1 - 1)_e = (\mathcal{A}_2 - 1)_e = 0. \tag{7.31}$$

This result is also in full agreement with our general theorem I in a somewhat more complicated example than given before. The two reactions of this sample show no Onsager coupling but again, this does not mean that the rate of one reaction is independent of the affinity of the other reaction. Equations (7.29) and (7.30) show how the rate of reaction 1 depends on the affinity of reaction 2, and vice versa. Of course, for higher order coefficients the RGRR-s are not valid.

d) *The triangle reaction scheme*

Let us turn now to the analysis of triangle reactions which represent the more simple stoichiometrically dependent network of reactions. In this case, of the three reactions

$$\begin{aligned} -M_1 + M_2 &= 0 \\ -M_2 + M_3 &= 0 \\ -M_3 + M_1 &= 0 \end{aligned}$$



(7.32)

only two are independent, since the rank of the matrix of the stoichiometric coefficients

$$\nu_{rk} = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 1 & 0 & -1 \end{pmatrix} \tag{7.33}$$

is equal to two.

Correspondingly, e.g., the equation of the third reaction can be obtained by linear combination of the other two equations

$$\beta_{13}(-M_1 + M_2) + \beta_{23}(-M_2 + M_3) = -M_3 + M_1 \tag{7.34}$$

with

$$\beta_{13} = \beta_{23} = -1.$$

Affinity A_3 of reaction 3 can be derived by the analogous linear combination

$$A_3 = \beta_{13} A_1 + \beta_{23} A_2 = -A_1 - A_2 \tag{7.35}$$

where A_1 and A_2 are the independent affinities. The independent thermodynamic fluxes are the following

$$I_1^* = I_1 + \beta_{13} I_3 = I_1 - I_3, \tag{7.36}$$

$$I_2^* = I_2 + \beta_{23} I_3 = I_2 - I_3. \tag{7.37}$$

It is emphasized, that I_1^* and I_2^* represent Onsagerian fluxes only, but not reaction rates. The independent reaction variables are obtained in a similar way

$$\Delta\xi_1^* = \Delta\xi_1 + \beta_{13}\Delta\xi_3 = \Delta\xi_1 - \Delta\xi_3, \tag{7.38}$$

$$\Delta\xi_2^* = \Delta\xi_2 + \beta_{23}\Delta\xi_3 = \Delta\xi_2 - \Delta\xi_3 \tag{7.39}$$

which are related to the deviations of the mole numbers from equilibrium values by the following equations

$$\Delta n_1 = \nu_{11}\Delta\xi_1^* + \nu_{12}\Delta\xi_2^* = -\Delta\xi_1^* + \Delta\xi_2^* \tag{7.40}$$

$$\Delta n_2 = \nu_{21}\Delta\xi_1^* + \nu_{22}\Delta\xi_2^* = -\Delta\xi_2^* \tag{7.41}$$

$$\Delta n_3 = \nu_{31}\Delta\xi_1^* + \nu_{32}\Delta\xi_2^* = \Delta\xi_1^*. \tag{7.42}$$

Consequently, equations of type (5.10) have the following form

$$\mathcal{A}_1 = \frac{1 - \dfrac{\Delta\xi_1^*}{n_1^e} + \dfrac{\Delta\xi_2^*}{n_1^e}}{1 - \dfrac{\Delta\xi_2^*}{n_2^e}}\,; \quad \mathcal{A}_2 = \frac{1 - \dfrac{\Delta\xi_2^*}{n_2^e}}{1 + \dfrac{\Delta\xi_1^*}{n_3^e}}$$

or rearranged

$$-\frac{1}{n_1^e}\Delta\xi_1^* + \left(\frac{1}{n_1^e} + \frac{\mathcal{A}_1}{n_2^e}\right)\Delta\xi_2^* = \mathcal{A}_1 - 1\,, \tag{7.43}$$

$$-\frac{\mathcal{A}_2}{n_3^e}\Delta\xi_1^* - \frac{1}{n_2^e}\Delta\xi_2^* \qquad = \mathcal{A}_2 - 1\,. \tag{7.44}$$

The solution of these equation system is in terms of the independently selected absolute affinities:

$$\Delta\xi_1^* = n_3^e \frac{n_1^e + n_2^e - n_2^e\mathcal{A}_2 - n_1^e\mathcal{A}_1\mathcal{A}_2}{n_3^e + n_2^e\mathcal{A}_2 + n_1^e\mathcal{A}_1\mathcal{A}_2,}\,, \tag{7.45}$$

$$\Delta\xi_2^* = n_2^e \frac{n_3^e - n_1^e\mathcal{A}_2 - n_3^e\mathcal{A}_2 + n_1^e\mathcal{A}_1\mathcal{A}_2}{n_3^e + n_2^e\mathcal{A}_2 + n_1^e\mathcal{A}_1\mathcal{A}_2}\,. \tag{7.46}$$

Finally, substituting equations (7.45) and (7.46) into the rate functions, we have

$$I_1 = I_1^e\left[1 + \frac{\Delta n_1}{n_1^e} - \left(1 + \frac{\Delta n_2}{n_2^e}\right)\right], \tag{7.47}$$

$$I_2 = I_2^e\left[1 + \frac{\Delta n_2}{n_2^e} - \left(1 + \frac{\Delta n_3}{n_3^e}\right)\right], \tag{7.48}$$

$$I_3 = I_3^e\left[1 + \frac{\Delta n_3}{n_3^e} - \left(1 + \frac{\Delta n_1}{n_1^e}\right)\right]. \tag{7.49}$$

Now, considering equations (7.36), (7.37) and (7.40)—7.42) and (7.45), (7.46) the nonlinear phenomenological equations between the independent fluxes I_1^*, I_2^* and the independent affinities A_1, A_2 are obtained in the form

$$I_1^* = n\,\frac{-I_3^e - I_1^e\exp\left(\frac{A_2}{RT}\right) + (I_1^e + I_3^e)\exp\left(\frac{A_1 + A_2}{RT}\right)}{n_3^e + n_2^e\exp\left(\frac{A_2}{RT}\right) + n_1^e\exp\left(\frac{A_1 + A_2}{RT}\right)} \tag{7.50}$$

$$I_2^* = n\,\frac{-I_2^e - I_3^e + I_2^e\exp\left(\frac{A_2}{RT}\right) + I_3^e\exp\left(\frac{A_1 + A_2}{RT}\right)}{n_3^e + n_2^e\exp\left(\frac{A_2}{RT}\right) + n_1^e\exp\left(\frac{A_1 + A_2}{RT}\right)} \tag{7.51}$$

where

$$n = n_1^e + n_2^e + n_3^e\,.$$

All linear and higher order coefficients can be evaluated by taking the equilibrium values of partial derivatives (7.17) of our general constitutive equations (7.50) and (7.51). For the Onsagerian coefficients

$$L_{11} = \frac{I_1^e + I_3^e}{RT}; \quad L_{22} = \frac{I_2^e + I_3^e}{RT}; \quad L_{12} = L_{21} = \frac{I_3^e}{RT} \tag{7.52}$$

which results are, of course, not new but represent only general forms. For the coefficients of higher order approximations, we have

$$\begin{aligned}
&L_{111} = \frac{I_1^e + I_3^e}{(RT)^2}(1 - 1x_1^e); \quad L_{222} = \frac{I_2^e + I_3^e}{(RT)^2}(2x_3{}' - 1);\\
&L_{112} = \frac{1}{(RT)^2}\left[I_1^e x_3^e + I_3^e(x_3^e - x_1^e)\right]; \quad L_{122} = \frac{I_3^e}{(RT)^2}(2x_3^e - 1);\\
&L_{211} = \frac{I_3^e}{(RT)^2}(1 - 2x_1^e); \quad L_{212} = \frac{1}{(RT)^2}\left[I_3^e(x_3^e - x_1^e) - I_2^e x_1^e\right]
\end{aligned} \tag{7.53}$$

and

$$L_{1111} = \frac{I_1^e + I_3^e}{(RT)^3}\,[1 - 6x_1^e + 6(x_1^e)^2]$$

$$L_{1112} = \frac{1}{(RT)^3}\,\big[I_1^e(1 - 5x_1^e - x_2^e + 4(x_1^e)^2 + 4x_1^e x_2^e) + {}$$

$$+ I_3^e(1 - 6x_1^e - x_2^e + 6(x_1^e)^2 + 4x_1^e x_2^e)\big]$$

$$L_{1122} = \frac{1}{(RT)^3}\,\big[I_1^e(1 - 3x_1^e - 3x_2^e + 2(x_1^e)^2 + 4x_1^e x_2^e + 2(x_2^e)^2) + {}$$

$$+ I_3^e(1 - 6x_1^e - 3x_2^e + 6(x_1^e)^2 + 8x_1^e x_2^e + 2(x_2^e)^2)\big] \tag{7.54}$$

$$L_{1222} = \frac{I_3^e}{(RT)^3}\,[1 - 6(x_1^e + x_2^e)\,x_3^e]\,;\; L_{2111} = \frac{I_3^e}{(RT)^3}\,[1 - 6x_1^e(1 - x_1^e)]$$

$$L_{2112} = \frac{1}{(RT)^3}\,\big[I_2^e x_1^e(1 + 2x_1^e) + I_3(1 - 6x_1^e - x_2^e + 6(x_1^e)^2 + 4x_1^e x_2^e)\big]$$

$$L_{2122} = \frac{1}{(RT)^3}\,\big[I_2^e(-3x_1^e + 4x_1^e x_2^e + 4(x_1^e)^2) + {}$$

$$+ I_3^e(1 - 6x_1^e - 3x_2^e + 6(x_1^e)^2 + 8x_1^e x_2^e + 2(x_2^e)^2)\big]$$

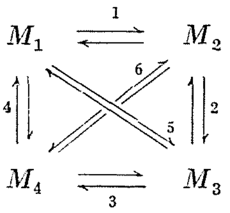
$$L_{2222} = \frac{I_2^e + I_3^e}{(RT)^3}\,[1 - 6(x_1^e + x_2^e) + 6(x_1^e + x_2^e)^2]$$

where x_k^e denotes equilibrium mole fraction of component k. The above expressions show that Onsager's reciprocal relations are now really satisfied, but only in the case of a stoichiometrically equivalent independent set of constitutive equations. Hence, the example of triangular reactions gives the simplest illustration of our general Theorem II., according to which, in a stoichiometrically dependent network of reactions for the stoichiometrically equivalent independent and reduced set of linear constitutive equations the ORR-s are satisfied in a real fashion. This means, in an entirely general sense, that as it is always possible to reduce a set of R-dependent chemical reactions into the form of a stoichiometrically equivalent but independent network of mechanism, it is possible to describe, at least in the linear theory, the kinetics of the original stoichiometrically dependent mechanism by a kinetically uncoupled set of linear rate equations if ORR-s are trivially satisfied or equivalently by a reduced set of kinetically coupled constitutive equations where ORR-s are satisfied in a real fashion.

e) *The reversible monomolecular reaction system of four components*

In the most general form for a coupled set of first order reactions every component is reacting to form every other component. This set is called a reversible monomolecular reaction system [31]. For four components

$$\begin{aligned}-M_1 + M_2 &= 0\\ -M_2 + M_3 &= 0\\ -M_3 + M_4 &= 0\\ -M_4 + M_1 &= 0\\ -M_1 + M_3 &= 0\\ -M_4 + M_2 &= 0\end{aligned} \tag{7.55}$$



are reactions and scheme of the system. The rank of the stoichiometric matrix

$$\nu_{kr} = \begin{pmatrix} -1 & 0 & 0 & 1 & -1 & 0\\ 1 & -1 & 0 & 0 & 0 & 1\\ 0 & 1 & -1 & 0 & 1 & 0\\ 0 & 0 & 1 & -1 & 0 & -1 \end{pmatrix} \tag{7.56}$$

is 3. Therefore, in the system there are three independent reactions. Let the first three reactions ($r' = 1, 2, 3$) be chosen as independent, the other three ($r'' = 4, 5, 6$) as dependent.

Reaction 4 can be obtained by linear combination of the first three reactions with the use of the coefficients $\beta_{14} = \beta_{24} = \beta_{34} = -1$. Reaction 5 is a linear combination of the first two reactions with the coefficients $\beta_{15} = \beta_{25} = 1$ and $\beta_{35} = 0$. Finally, reaction 6 is a linear combination of reactions 2 and 3 with the coefficients $\beta_{16} = 0$ and $\beta_{26} = \beta_{36} = -1$.

According to equation (4.9), the independent Onsagerian fluxes are the following

$$\begin{aligned} I_1^* &= I_1 + \sum_{r''=4}^{6} \beta_{1r''} I_{r''} = I_1 - I_4 + I_5,\\ I_2^* &= I_2 + \sum_{r''=4}^{6} \beta_{2r''} I_{r''} = I_2 - I_4 + I_5 - I_6,\\ I_3^* &= I_3 + \sum_{r''=4}^{6} \beta_{3r''} I_{r''} = I_3 - I_4 - I_6. \end{aligned} \tag{7.57}$$

For the deviation from equilibrium we obtain

$$\begin{aligned} \Delta n_1 &= -\Delta\xi_1^*; & \Delta n_2 &= \Delta\xi_1^* - \Delta\xi_2^*;\\ \Delta n_3 &= \Delta\xi_2^* - \Delta\xi_3^*; & \Delta n_4 &= \Delta\xi_3^*. \end{aligned} \tag{7.58}$$

For the three affinities A_1, A_2, A_3 selected as independent (more precisely, for the absolute affinities $\mathcal{A}_1 = e^{\frac{A_1}{RT}}$, etc.) we have the following equations of type (5.10)

$$-\left(\frac{1}{n_1^e}+\frac{\mathcal{A}_1}{n_2^e}\right)\Delta\xi_1^*+\frac{\mathcal{A}_1}{n_2^e}\Delta\xi_2^* =\mathcal{A}_1-1$$

$$\frac{1}{n_2^e}\Delta\xi_1^*-\left(\frac{1}{n_2^e}+\frac{\mathcal{A}_2}{n_3^e}\right)\Delta\xi_2^*+\frac{\mathcal{A}_2}{n_3^e}\Delta\xi_3^*=\mathcal{A}_2-1$$

$$\frac{1}{n_3^e}\Delta\xi_2^*-\left(\frac{1}{n_3^e}+\frac{\mathcal{A}_3}{n_4^e}\right)\Delta\xi_3^*=\mathcal{A}_3-1. \qquad (7.59)$$

This linear equation system has the solutions

$$\Delta\xi_1^*=n_1^e\frac{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3-(n_2^e+n_3^e+n_4^e)\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_2+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$\Delta\xi_2^*=\frac{n_1^en_4^e+n_2^en_4^e+(n_1^en_3^e+n_2^en_3^e)\mathcal{A}_3-(n_2^en_3^e+n_2^en_4^e)\mathcal{A}_2\mathcal{A}_3-(n_1^en_3^e+n_1^en_4^e)\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3} \qquad (7.60)$$

$$\Delta\xi_3^*=n_4^e\frac{n_1^e+n_2^e+n_3^e-n_2^e\mathcal{A}_3-n_2^e\mathcal{A}_2\mathcal{A}_3-n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

which characterize the deviation from equilibrium in independent reaction representation. In component representation, according to equations (6.10)

$$\Delta n_1=n_1^e\frac{-n_4^e-n_3^e\mathcal{A}_3-n_2^e\mathcal{A}_2\mathcal{A}_3+(n_2^e+n_3^e+n_4^e)\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$\Delta n_2=n_2^e\frac{-n_4^e-n_3^e\mathcal{A}_3+(n_1^e+n_3^e+n_4^e)\mathcal{A}_2\mathcal{A}_3-n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_2\mathcal{A}_1\mathcal{A}_3}$$

$$\Delta n_3=n_3^e\frac{-n_4^e+(n_1^e+n_2^e+n_4^e)\mathcal{A}_3-n_2^e\mathcal{A}_2\mathcal{A}_3-n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3} \qquad (7.61)$$

$$\Delta n_4=n_4^e\frac{n_1^e+n_2^e+n_3^e-n_3^e\mathcal{A}_3-n_2^e\mathcal{A}_2\mathcal{A}_3-n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}\,.$$

Substituting these into the six kinetic equations of the form (5.13), we obtain the rates of all reactions

$$I_1=I_1^e\left[1+\frac{\Delta n_1}{n_1^e}-\left(1+\frac{\Delta n_2}{n_2^e}\right)\right]=I_1^e n\,\frac{-\mathcal{A}_2\mathcal{A}_3+\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$I_2=I_2^e\left[1+\frac{\Delta n_2}{n_2^e}-\left(1+\frac{\Delta n_3}{n_3^e}\right)\right]=I_2^e n\,\frac{-\mathcal{A}_3+\mathcal{A}_2\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$I_3=I_3^e\left[1+\frac{\Delta n_3}{n_3^e}-\left(1+\frac{\Delta n_4}{n_4^e}\right)\right]=I_3^e n\,\frac{-1+\mathcal{A}_3}{n_4^e+n_3^e\mathcal{A}_3+n_2^e\mathcal{A}_2\mathcal{A}_3+n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3} \qquad (7.62)$$

$$I_4 = I_4^e\left[1 + \frac{\Delta n_4}{n_4^e} - \left(1 + \frac{\Delta n_1}{n_1^e}\right)\right] = I_4^e n \frac{1 - \mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e + n_3^e\mathcal{A}_3 + n_2^e\mathcal{A}_2\mathcal{A}_3 + n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$I_5 = I_5^e\left[1 + \frac{\Delta n_1}{n_1^e} - \left(1 + \frac{\Delta n_3}{n_3^e}\right)\right] = I_5^e n \frac{\mathcal{A}_3 - \mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}{n_4^e + n_3^e\mathcal{A}_3 + n_2^e\mathcal{A}_2\mathcal{A}_3 + n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3}$$

$$I_6 = I_6^e\left[1 + \frac{\Delta n_4}{n_4^e} - \left(1 + \frac{\Delta n_2}{n_2^e}\right)\right] = I_6^e n \frac{1 - \mathcal{A}_2\mathcal{A}_3}{n_4^e + n_3^e\mathcal{A}_3 + n_2^e\mathcal{A}_2\mathcal{A}_3 + n_1^e\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3} \tag{7.62}$$

where $n = n_1^e + n_2^e + n_3^e + n_4^e$.

Finally, the independent Onsagerian fluxes are obtained by combination of equations (7.57) and (7.62)

$$I_1^* = n\,\frac{-I_4^e - I_5^e e^{\frac{A_3}{RT}} - I_1^e e^{\frac{A_2+A_3}{RT}} + (I_1^e + I_4^e + I_5^e)\, e^{\frac{A_1+A_2+A_3}{RT}}}{n_4^e + n_3^e e^{\frac{A_3}{RT}} + n_2^e e^{\frac{A_2+A_3}{RT}} + n_1^e e^{\frac{A_1+A_2+A_3}{RT}}}$$

$$I_2^* = n\,\frac{-(I_4^e + I_6^e) - (I_2^e + I_5^e)\, e^{\frac{A_3}{RT}} + (I_2^e + I_6^e)\, e^{\frac{A_3+A_2}{RT}} + (I_4^e + I_5^e)\, e^{\frac{A_1+A_2+A_3}{RT}}}{n_4^e + n_3^e e^{\frac{A_3}{RT}} + n_2^e e^{\frac{A_2+A_3}{RT}} + n_1^e e^{\frac{A_1+A_2+A_3}{RT}}} \tag{7.63}$$

$$I_3^* = n\,\frac{-(I_3^e + I_4^e + I_6^e) + I_3^e e^{\frac{A_3}{RT}} + I_6^e e^{\frac{A_2+A_3}{RT}} + I_4^e e^{\frac{A_1+A_2+A_3}{RT}}}{n_4^e + n_3^e e^{\frac{A_3}{RT}} + n_2^e e^{\frac{A_2+A_3}{RT}} + n_1^e e^{\frac{A_1+A_2+A_3}{RT}}}\,.$$

These are the nonlinear phenomenological flux-force relations of the kinetic system (7.55). By taking the equilibrium values of the partial derivatives with respect to the independent affinities the matrix of Onsager's coefficients is obtained as:

$$L_{rs} = \frac{1}{RT}\begin{pmatrix} I_1^e + I_4^e + I_5^e & I_4^e + I_5^e & I_4^e \\ I_4^e + I_5^e & I_2^e + I_4^e + I_5^e + I_6^e & I_4^e + I_6^e \\ I_4^e & I_4^e + I_6^e & I_3^e + I_4^e + I_6^e \end{pmatrix} \tag{7.64}$$

which is symmetric. Hence, the Onsager reciprocal relations are again really satisfied for the stoichiometrically equivalent independent set of linear equations, in full agreement with our general Theorem II.

Higher order approximations of the constitutive equations are not presented here, since at this stage Rysselberghe GRR-s are not valid again.

8. Facts and hopes

Relying on the results reported and recording some facts their fatal consequences are intended to be pointed out. Finally, in conclusion of this paper, comments are made on new possibilities and pathways for expounding a nonlinear thermodynamic theory of reaction kinetics.

Let us consider first the facts. It is surprising that a survey of the literature over a half a century following the pioneering papers of Onsager published in 1931 shows that only three basic results can be recorded pertaining to the consistency of reaction kinetics with thermodynamics. These results are the following:

Theorem I: *For every stoichiometrically independent network of elementary chemical reactions in the linear domain of constitutive equations the ORR-s are satisfied in a trivial way* .

Theorem II: *In every stoichiometrically dependent network of elementary chemical reactions for the stoichiometrically equivalent independent set of linear constitutive equations the ORR-s are satisfied in a real fashion.*

Theorem III: *The Rysselberghe type nonlinear thermodynamic theory of chemical reactions, i.e., the theory in which, through constitutive equations, the reaction rates are expressed as nonlinear functions of the affinities, is inconsistent with the classical theory of chemical kinetics.*

Theorem I and Theorem II have been discussed and derived in Sections 6a) and 6b), respectively. As precursors to this derivation references [7], [44] and [46] should be mentioned in which — and also in other papers — some details have already been mentioned. At any rate, having derived and clearly and generally formulated Theorem I and Theorem II, we think that consistency of the linearized form of the Guldberg—Waage kinetics with the linear Onsager theory is fully proven. It is emphasized that application of the linear theory to chemical kinetics is of great importance in spite of views denying it.

The validity of Theorem III must be accepted, since WEI and ZAHNER's and OLÁH's particular remarks and the general studies of BATAILLE, EDELEN and KESTIN and our perhaps more general results illustrated through several examples show that nonlinear thermodynamics in its present form is inconsistent with the classical theory of reaction kinetics.

As to the validity of Theorem III., the following questions must be raised.

(a) Has the Guldberg—Waage form of chemical kinetics to be essentially modified?

(b) Could the laws of thermodynamics or any of them be incorrect?

(c) May be assumed that function $(e^{\frac{A}{RT}} - 1)$ in the Marcelin—De Donder equation cannot be approximated by its Taylor series to higher than first degree?

Naturally, all these questions will receive a negative answer, since chemical kinetics and thermodynamics are both well established and experimentally proven theories. Not to speak of Taylor's series. The only conclusion we can arrive at is that Theorem III is not valid. However, examples 7b) and 7d) show that Theorem III is certainly valid. Consequently, the contradiction has to be faced that chemical kinetics, i.e. the evolution of the concentrations of chemical species in kinetic systems does not seem to be governed by the general principles of physics (i.e., thermodynamics) with the exception of the linear domain. This contradiction must be solved.

It is pointed out here that Theorem III is not a statement on the inconsistency of chemical kinetics with nonlinear thermodynamics in general, but only with the Rysselberghe-type nonlinear theory. The inconsistency seems to be eliminable by a proper choice of thermodynamic forces instead of the affinities. A proper choice is always of fundamental importance and cannot be substituted by formal mathematical manipulations. E.g., it was the improper mathematical manipulations [34] which moved MEIXNER to republish [48] his transformation theorems [6] thirty years after the first publication [47].

Concerning the question of consistency of chemical kinetics with nonlinear thermodynamics the situation is as follows. The theory formulated independently by Gyarmati and by Li has been neglected or misinterpreted in later publications of other authors. The chaotic situation may be due to the fact that Rysselberghe and later other authors — although they knew the original papers [16—19] — made no reference to them and elaborated theories including only new errors. Misinterpretation of the old theory led — in the case of chemical kinetics — from equations (9) and (10) to equations (15) and (16) by assuming the identity $X_i \equiv A_i$.

In the application to chemical kinetics neither Li nor Gyarmati have ever proposed the GRR-s (9) in the form (15) or the constitutive equations (10) in the form (16). Neither of them have ever stated that affinities are real thermodynamic forces in chemical kinetics in the nonlinear domain!

In conclusion it is to be stated that *in the nonlinear domain affinities are not the real forces of chemical reactions, and for this reason nonlinear thermodynamic theories using reaction rate — affinity constitutive equations must be inconsistent with chemical kinetics.* The Gyarmati—Li theory allows other choices for thermodynamic forces which properly chosen must make nonlinear thermodynamics consistent with reaction kinetics. Our current studies are aimed at finding this correct choice.

Summary

The authors intend to contribute to the solution of the problems posed by the inconsistency of nonlinear thermodynamics with the classical theory of chemical kinetics. It was necessary to subject old and new nonlinear thermodynamic theories to profound analysis. A relatively long introduction was devoted to this analysis. Then thermodynamic basic equations of homogeneous closed systems are presented and stoichiometric equations of chemical reactions in such systems are discussed. Direct transformation of stoichiometrically dependent reaction network into a stoichiometrically equivalent independent system is also given. As a next step the authors calculated the nonlinear constitutive equations of reaction kinetics for any stoichiometrically independent system and presented the transformation between dependent and independent systems. In addition to affinities, they introduced the concept of absolute affinities, which seems to have fundamental importance for the nonlinear theory. A simple method is proposed to solve the algebraic equations between reaction coordinates and absolute affinities. This method allows calculation of the reaction rates as nonlinear functions of the affinities. Returning to the linear Onsager theory authors prove that in stoichiometrically independent systems the ORR-s are always trivially satisfied. A real satisfaction of the ORR-s occurs only in case of such independent fluxes and affinities that equivalently represent dependent systems. Finally, the general theory is applied to the examples of systems of stoichiometrically separated reactions, of consecutive reactions and to triangle and quadrangle reaction schemes. The constitutive equations between reaction rates and affinities are expanded in series to first, second and third degrees and the corresponding chemical drag coefficients are calculated. It turned out that the RGRR-s are not satisfied in higher than first degrees. This is equivalent to the fact that the Rysselberghe type nonlinear theories are inconsistent with chemical kinetics. The reason for this critical situation is analyzed and the authors express their view that the inconsistency of chemical kinetics with thermodynamics cannot be accepted and, for the thermodynamic forces another choice should be made to replace the affinities, which are not the true thermodynamic forces in the nonlinear realms.

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dr. István GYARMATI H—1521 Budapest, XI., Budafoki út 6—8.
dr. Sándor LENGYEL H—1025 Budapest, Pusztaszeri u. 57.