

An Unifying Thermodynamic Framework for Nonlinear Macrokinetics in Reaction-Diffusion Systems

Stanislaw SIENIUTYCZ
Warsaw University of Technology
Faculty of Chemical and Process Engineering, Department of Process Separation
1 Waryńskiego Street (room 232), 00-645 Warsaw, Poland
E-mail: sieniutycz@ichip.pw.edu.pl

Abstract

Two competing directions in elementary chemical or transport steps are analyzed from the viewpoint of their contribution to the overall rates. Systems with nonlinear transport phenomena and chemical reactions are described by the equations of nonlinear kinetics of the Marcelin-Kohnstamm-de Donder type that contain terms exponential with respect to the Planck potentials and temperature reciprocal. Simultaneously these equations are analytical expressions characterizing the transport of the substance or energy through the energy barrier. They constitute potential representations of a generalized law of mass action that includes the effect of transfer phenomena and external fields. Important are the physical consequences of these kinetics near and far from equilibrium. In these developments nonlinear symmetries and generalized affinity are important. The affinity picture - new for transport phenomena - and the traditional Onsagerian picture are shown to constitute two equivalent representations for kinetics of chemical reactions and transfer processes. Correspondence with the Onsager's theory is shown closely to the thermodynamic equilibrium. Yet, it can be shown that rates of transport processes and chemical reactions far-from-equilibrium cannot be determined uniquely in terms of their affinities since these rates depend on all state coordinates of the system.

Keywords: Chemical kinetics, mass action, transport phenomena, generalised affinity

1. Introduction

The basic idea of the present work can easily be perceived after comparing rate equations describing microscopic and macroscopic processes. Tolman's law of microscopic reversibility (Waldram, 1984) states that for elementary ("microscopic") interactions the constant parameters (the probability factors) in the rate equations of the reverse processes are equal:

$$P_{i \rightarrow k} = P_{k \rightarrow i} \quad (1)$$

Consequently, when elementary processes with elastic collisions of molecules take place, the microscopic rate equations are identical for direct and reverse processes. The law of microscopic reversibility is thus equivalent with the statement that the rate coefficients of competing micro-processes are the same, or that $k^f = k^b$, where indices f and b refer to forward and backward

rates, so that the equilibrium constant equals to unity $K = k^f/k^b = 1$.

However, for macroscopic (e.g., chemical reaction) processes this property is no longer valid. The standard structure of the kinetic law of mass action (KMAL) treats the (net) rate of a reaction as the difference of two competing unidirectional fluxes, each flux being expressed in terms of the concentrations \mathbf{c} and the temperature T . For a net chemical rate of a single reaction $J = r^f(\mathbf{c}^f) - r^b(\mathbf{c}^b)$. The consequence of this description is that the ratio $K = k^f/k^b$ or the equilibrium constant can assume very diverse values.

To ensure the agreement between the descriptions of macroscopic and microscopic processes some researchers (Waldram, 1984; Lengyel and Gyarmati, 1986; Keizer, 1987; Lengyel, 1988; in particular Oláh, 1997a,b, 1998), have proposed in a series of works that the familiar mass-action expressions for the net

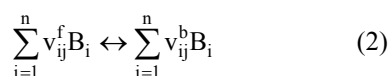
reaction rate, $r = r^f(\mathbf{c}^f) - r^b(\mathbf{c}^b)$, should be replaced by the so-called potential-action laws (PA laws) where rate expressions are in terms of the potentials $1/T$, $-\mu_i/T$, etc., i.e. the quantities that equalize at equilibrium rather than concentrations \mathbf{c} . Truncated forms of these expressions have proved its utility in the analysis of currents of photons and electrons in semiconductors as elements of solar cells. The idea of use of intensive variables in thermodynamic descriptions was extensively promoted by Callen (1985) in the fluctuation theory.

Typically, potential-based equations contain exponential terms with Planck potentials and temperature reciprocal, and they can be related to analytical expressions characterizing the jump through the energy barrier as used in Eyring's theory of rate processes (Glasstone et al., 1941).

To show how potential-based equations appear we shall transform to the space of potentials the basic equations of chemical kinetics taken in their usual form. This usual form represents the so-called kinetic mass action law (KMAL) or the Guldberg and Waage (1867) kinetics, (Sieniutycz, 1987). As this classical formal structure of KMAL was confirmed by a very large number of experiments in chemical kinetics, it constitutes the suitable starting point to transformations and generalizations. Firstly, rate processes subject to the restriction of isothermal kinetics are considered. They will be transformed from the usual space of concentrations to the space of Planck potentials as thermodynamic intensities, as shown below.

2. Potential Representation of Classical Kinetics of Rate Processes

Consider the system of chemical reactions:



$i = 1, 2, \dots, n$ and $j = 1, 2, \dots, N$, involving the chemical components B_k ($k=1, \dots, n$) and proceeding at the rates r_1, \dots, r_N . The unidirectional stoichiometric coefficients for forward and backward rates are always positive quantities. The reaction is the competition of forward and backward processes. Using the usual structure of chemical potentials

$$\mu_i(\mathbf{c}_i, T) = \mu_{i0}(T) + RT \ln c_i$$

concentrations c_i in the form

$$c_i = \exp\left(\frac{\mu_i}{RT}\right) \exp\left(-\frac{\mu_{i0}}{RT}\right) \quad (3)$$

are substituted into the classical mass action kinetic

$$J_j = r_j^f - r_j^b = k_j^f(T) \prod_{i=1}^n c_i^{v_{ij}^f} - k_j^b(T) \prod_{i=1}^n c_i^{v_{ij}^b} \quad (4)$$

The result is the chemical rate equation in the Marcelin-de Donder form

$$J_j(\mathbf{c}, T) = r_j^f(\mathbf{c}, T) - r_j^b(\mathbf{c}, T) \\ = r_j^0(T) \left(\exp \sum_{i=1}^n v_{ij}^f \frac{\mu_i}{RT} - \exp \sum_{i=1}^n v_{ij}^b \frac{\mu_i}{RT} \right) \quad (5)$$

This equation already has the typical (while still not the most general) nonlinear structure of macro-kinetic equations. Its virtue is the single (universal) reaction rate constant, representing the so-called exchange current, and the explicit satisfaction of the principle of microscopic reversibility at the state of thermodynamic equilibrium. The exchange current expressed by "usual" reaction rate constants has the form:

$$r_j^0(T) \equiv k_j^f(T) \left(\exp \sum_{i=1}^n -v_{ij}^f \frac{\mu_{i0}}{RT} \right) = \\ k_j^b(T) \left(\exp \sum_{i=1}^n -v_{ij}^b \frac{\mu_{i0}}{RT} \right) \quad (6)$$

In the case of ionic systems, electrochemical potentials should replace chemical potentials. In all considered cases equations obtained are analytical expressions characterizing the transport of the substance or energy through the energy barrier. They constitute potential representations of a generalized law of mass action that includes the effect of transfer phenomena and external fields.

Electrochemistry is, in fact, the realm where the notion of the exchange current is best known, *Figures 1 and 2*. Olah, in particular (1997a,b, 1998), has given suitable pictures that interpret anodic and cathodic currents as well as the exchange current in terms of voltage or electrochemical potential. In fact, it is the condition of the vanishing electrochemical affinity at equilibrium that makes it possible to define the universal rate constant r_j^0 or the exchange current of electrochemistry.

In the case of isothermal electrochemistry, the result of the procedure involving potential descriptions of kinetics is the Butler-Volmer equation that describes the electric current J as the resulting difference between the anodic and cathodic currents.

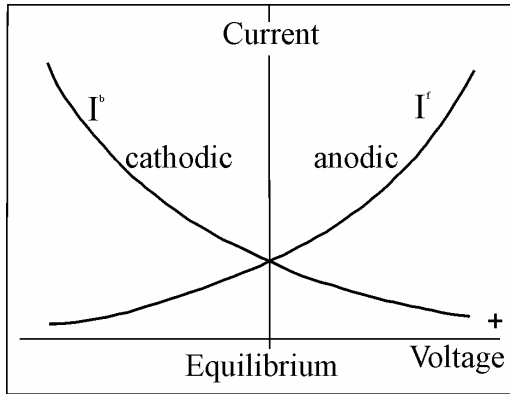


Figure 1. Oláh's interpretation of anodic and cathodic currents as well as of the exchange current in terms of voltage. Abscissa of crossing point of both currents describes the exchange current.

The potential form of the Butler-Volmer equation is:

$$J_{el} = I^{anod}(\mathbf{c}, T) - I^{cathod}(\mathbf{c}, T) \\ = I^0(T) \left(\exp \sum_{i=1}^n v_i^f \frac{\tilde{\mu}_i}{RT} - \exp \sum_{i=1}^n v_i^b \frac{\tilde{\mu}_i}{RT} \right) \quad (7)$$

where tilde symbols refer to electrochemical rather than chemical potentials.

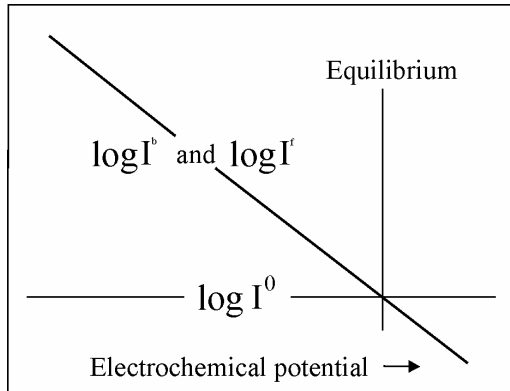


Figure 2. Interpretation of logarithms of anodic and cathodic currents as well as of the exchange current in terms of electrochemical potential.

Whereas the customary, equivalent form of the Butler-Volmer equation (Bockriss and Drazic, 1972) describes the electric current of a cell in terms of the overvoltage η

$$J_{el} = I^0 (\exp((1-\alpha)F\eta/RT) - \exp(-\alpha F\eta/RT)) \quad (8)$$

where J_{el} is electric current, α constant coefficient, η overvoltage and F universal Faraday's constant. The coefficient α

characterizes the symmetry of the energy barrier and is near to $1/2$. Equation (8), commonly used to describe various electrochemical systems including fuel cells, has been investigated most recently.

More information about the electrode kinetics can be found in references (Olah, 1997b; Bockriss and Drazic, 1972). A generalization of the above theoretical scheme using general principles of thermodynamics is now discussed.

3. Thermodynamic Generalization

In the potential-action laws both unidirectional (absolute) rates are expressed as functions of the potentials $F_i = (1/T, -\mu_i/T)$, $i=0, 1, \dots, n$, which are the thermodynamic conjugates of the extensive variables in the Gibbs equation for the system's entropy

$$dS = T^{-1}dE - \sum_{\alpha} T^{-1}\mu_{\alpha}dc_{\alpha} \equiv \sum_{i=0}^s F_i dC_i \equiv \mathbf{F} \cdot d\mathbf{C} \quad (9)$$

where $\mathbf{C} = (E, \mathbf{c})$ is a generalized state vector. Momentum terms are ignored and exchange processes of energy and substance at mechanical equilibrium are considered. The description used here is discrete, with finite driving forces, thus the continuous (field) description operating with gradients does not apply. The description that refers to the transport rather than rate processes is begun with. In this description the current associated with i -th degree of freedom is described by functions $I_i^f(F_0, F_1, \dots, F_s)$ and $I_i^b(F_0, F_1, \dots, F_s)$. By assumption the potentials F_i include effects of external fields. At thermal and diffusive equilibrium the two vector equalities are valid

$$(\mathbf{F}^f)_{eq} = (\mathbf{F}^b)_{eq} = (\mathbf{F})_{eq} \quad (10)$$

$$\mathbf{I}^f(F_0, F_1, \dots, F_s)_{eq} = \mathbf{I}^b(F_0, F_1, \dots, F_s)_{eq} \quad (11)$$

These two equations can simultaneously be valid only if the rate vectors \mathbf{I}^f and \mathbf{I}^b describing the direct and reverse currents of the quantities 0, 1, 2...s are of the same form in the directions f and b . (Still, the expressions describing the resulting rates can be quite diverse.) A corollary is valid: both unidirectional flows of a particular quantity k are described by the same function $I_j(F_0, F_1, \dots, F_s)$.

Using the standard formalism elaborated for a set of chemical reactions

$$\sum_{k=0}^s v_{ki}^f B_k^f \leftrightarrow \sum_{k=0}^s v_{ik}^b B_k^b \quad (12)$$

($i, k = 0, 1, 2, \dots, s$ and zero refers to the energy) here the $s+1$ exchange processes as peculiar chemical reactions described by quadratic

(generally non-symmetric) matrices of stoichiometric type v_{ik}^f and v_{ik}^b that satisfy the equality are considered:

$$v_{ik}^f = v_{ik}^b \equiv v_{ik}^* \quad (13)$$

Nothing can be said about the symmetry properties of this matrix. As in this case the resulting (net) coefficients $v_{ik} = v_{ik}^b - v_{ik}^f$ always vanish, we shall call v_{ik}^f and v_{ik}^b peculiar stoichiometric coefficients. The equality $v_{ik}^f = v_{ik}^b$ assures the thermodynamic equilibrium in exchange processes whenever all potentials F_k are the same at states f and b , i.e. for $\mathbf{F}_{eq}^f = \mathbf{F}_{eq}^b$. In genuine chemical reactions stoichiometric matrices v_{ik}^f and v_{ik}^b are in general not quadratic matrices, and they are unequal in states f and b , the property that ensures the uniqueness of chemical equilibria. It will soon be seen that the symmetry properties in the system (assuring satisfaction of the Onsager's reciprocity relations) are represented by the following equality:

$$I_i^{eq} v_{ki}^* = I_k^{eq} v_{ik}^* \quad (14)$$

Using the standard formalism of chemical reaction systems (Sieniutycz, 1987; Shiner, 1987), for each exchange process a general affinity can be postulated that satisfies some essential relationships written out below.

For an uncoupled process

$$A_k^s = v_k^b F_k^b - v_k^f F_k^f = R \cdot \left\{ \ln \left[\frac{(k_k^f C_k^{f_i})}{(k_k^b C_k^{b_i})} \right] \right\} = R \ln(I_k^f / I_k^b) \quad (15)$$

where, in this case, trivially, $v_k^f = v_k^b = 1$. This means that any uncoupled kinetics represents, in fact, a first order kinetics. The same final expression holds true for a general coupled process

$$A_k^s = \sum_i v_{ik}^b F_i^b - \sum_i v_{ik}^f F_i^f = R \ln \left(\frac{(k_k^f \prod_{i=0}^s C_i^{f_{v_{ik}^f}})}{(k_k^b \prod_{i=0}^s C_i^{b_{v_{ik}^b}})} \right) = R \ln(I_k^f / I_k^b) \quad (16)$$

The quantity $A_k^s = A_k / T$ is the affinity of the k -th exchange process in the entropy representation. Only in the first (uncoupled) are scheme exchange processes governed by a trivial kinetics; in the second scheme the kinetics is quite involved. Still the last expression of the above equations does apply to exchange processes of any order (it is also valid for genuine chemical reactions). The above formulae show that any

finite affinity persisting in an irreversible process yields a constraint on forward and backward currents. The constraint means that in order to assure a positive net rate of exchange $J_k = I_k^f - I_k^b$, the forward rate must exceed the backward one according to the formula

$$I_k^f = I_k^b \exp(A_i^s / R) \quad (17)$$

This formula is well known in the realm of chemical reactions, where it is usually presented in an equivalent form describing the net reaction rate (Prigogine, 1959)

$$J_k = I_k^b(C) \{ \exp(A_k^s / R) - 1 \} \quad (18)$$

Its advantage is that it shows the proportionality of the net rate I_k to the affinity in the regime close to equilibrium, where I_k^b becomes a constant (due to the constancy of $\mathbf{C} = \mathbf{C}_{eq}$) and the affinity is small. Yet this formula also shows that far from equilibrium the transport rates cannot be determined uniquely in terms of their affinities because these rates depend on all state coordinates \mathbf{C} .

4. Properties of Generalized Exchange Equations

Due to the logarithmic structure of Planck potentials with respect to concentrations, the mathematical structure of the absolute (unidirectional) rates in terms of potentials $\mathbf{F} = (1/T, -\mu_i/T)$ also follows in an exponential form. The basic quantities of the rate theory are two unidirectional (absolute) currents $\mathbf{I}^f(\mathbf{F}^f)$ and $\mathbf{I}^b(\mathbf{F}^b)$, in fact $\mathbf{I}(\mathbf{F}^f)$ and $\mathbf{I}(\mathbf{F}^b)$, and potentials $\mathbf{F} = (1/T, -\mu_i/T)$. For $1, 2, \dots, s$ the subscript i refers to the species (charged or neutral), whereas the 0-th component refers to the energy. Unlike in Onsager's description, the differences in F_k play a secondary role; the basis is a relation linking absolute fluxes I_k with transfer potentials F_i . For an i -th forward process the following relation holds

$$I_k^f = I_k^0 \exp(-\sum_k v_{ik}^* F_i^f / R) \quad (19)$$

With appropriate indices the same is valid for the backward process. The exchange mechanism follows as the net result of the opposite effects. At the thermodynamic equilibrium both absolute rates and potentials F_k equalize, although they are different at nonequilibrium. The quantities I_k^0 ("exchange current") and v_{ik}^* (peculiar stoichiometric coefficients) are common for both directions. The net exchange flux corresponding to equation (19) is

$$J_k = I_k^0 \left\{ \exp\left(-\sum_i v_{ik}^* F_i^f / R\right) - \exp\left(-\sum_i v_{ik}^* F_i^b / R\right) \right\} \quad (20)$$

whereas the ratio of absolute fluxes is

$$I_k^f / I_k^b = \exp\left(\sum_i (v_{ik}^* F_i^b - v_{ik}^* F_i^f) / R\right) \quad (21)$$

In the considered case of $v_{ik}^f = v_{ik}^b \equiv v_{ik}^*$ the last formula is equivalent to the affinity-flux relation $I_j^f = I_j^b \exp(A_j^s / R)$, equation (18), discussed earlier. For the genuine chemical reactions the formulas analogous to equations (20) and (21) are given by equations (45) and (17). equations (20) and (21) show that the unidirectional (forward and backward) kinetics of transport processes are governed by the forward and backward l components of the extended affinities. For forward rates

$$\Pi_k^f \equiv \sum_i (v_{ik}^* F_i^f / R)$$

and, for backward ones

$$\Pi_k^b \equiv \sum_i (v_{ik}^* F_i^b / R).$$

In relation to the energy barrier, these quantities are defined for initial and final states of the exchange process. In fact, in the transport kinetics, they play the same role as the temperature does in the heat exchange; each i -th elementary transport proceeds in the direction from higher Π_i^f to lower Π_i^b . Therefore Π_k^f and Π_k^b are the “potentials of exchange”. An essential, interesting difference between equations (20) and (21) can now be stressed. Equation (20) proves that the resulting rate follows as the difference of (exponential) functions of Π_k , whereas equation (21) shows that the ratio of unidirectional rates is governed by (exponential) function of the differences $\Pi_k^f - \Pi_k^b$. The distinction between the kinetics in terms of “difference of functions” and “functions of differences” is useful to explain the violation of uniformity of optimal driving forces in the nonlinear problems of finite time thermodynamics obeying the kinetics of “difference of functions”. See *Figure 3*. Here it is stressed that the conventional description of irreversible processes (Onsager, 1931) uses net thermodynamic fluxes J_i and (net) thermodynamic forces X_i which are the differences of potentials F_i . Namely, the traditional rate equations (for example, those of the Onsager’s theory) are postulated as the relations of the following structure [5]-[8]

$$\mathbf{J} = \mathbf{f}(\mathbf{X}), \quad \mathbf{J} = -\Delta\mathbf{I}; \quad \mathbf{X} = \Delta\mathbf{F} \quad (22)$$

In the Oscanger’s (1939) theory

$$J_i = \sum_k L_{ik} X_k \quad (23)$$

where L_{ik} is an Onsagerian phenomenological coefficient. In the cases far from equilibrium this sort of equation is often non-unique. See the corresponding remark concerning the non-uniqueness of the transport rates in terms of their affinities, at the end of Section 3.

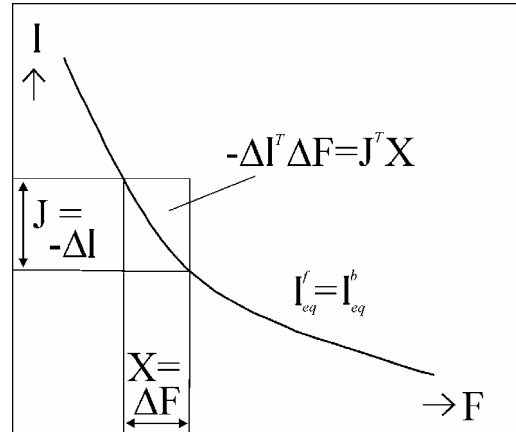


Figure 3. Interpretation of net fluxes \mathbf{J} and classical driving forces \mathbf{X} .

In the nonlinear approach of the present work two competing directions of the rate or transport process are always considered. In fact, thermodynamic nonequilibrium systems are described by the generalized Marceline-de Donder equations of nonlinear kinetics as first stated by Keizer (1987) and Hungarian researchers (Lengyel and Gyarmati, 1981, 1986; Lengyel, 1988), in particular Olah (1997a,b, 1998). These equations contain terms that are exponential with respect to Planck chemical potentials and T^{-1} , and simultaneously are analytical expressions characterizing the motion through the energy barrier (Glasstone et al., 1941).

Cross symmetry property can be tested as the symmetry condition for the matrix of the partial derivatives of fluxes with respect to potentials. The derivatives are calculated

$$\frac{\partial I_i}{\partial F_k} \equiv -L_{ik} = -I_i^0 \exp\left(-\sum_k v_{ki}^* F_k / R\right) v_{ki}^* / R \quad (24)$$

and

$$\frac{\partial I_k}{\partial F_i} \equiv -L_{ki} = -I_k^0 \exp\left(-\sum_i v_{ik}^* F_i / R\right) v_{ik}^* / R \quad (25)$$

The equality of these derivatives describes the general symmetry of nonlinear thermodynamics

$$\frac{\partial I_i}{\partial F_k} \equiv -L_{ik} = -I_i v_{ki}^* / R = -I_k v_{ik}^* / R = -L_{ki} \equiv \frac{\partial I_k}{\partial F_i} \quad (26)$$

Thus one can write the symmetry condition in the form

$$I_i v_{ki}^* = I_k v_{ik}^* \quad (27)$$

In particular, at equilibrium $I_i^{\text{eq}} v_{ki}^* = I_k^{\text{eq}} v_{ik}^*$. In this formalism symmetric rate coefficients are partial derivatives of absolute process rates with respect to the potentials (Olah, 1997a). Because such symmetry is experimentally proved and there are also statistical mechanics examples that show its validity, it can be regarded as the evidence of the theory correctness. This symmetry is not confined to linear rate relations. At the linear approximation the considered derivatives are the negative Onsagerian phenomenological coefficients ($-L_{ik} = -L_{ki}$). On the other hand, the matrix of peculiar stoichiometric coefficients is not symmetric.

$$-\frac{\partial \ln I_i}{\partial F_k} = v_{ki}^* \neq v_{ik}^* = -\frac{\partial \ln I_k}{\partial F_i} \quad (28)$$

When the process runs close to the equilibrium it is suitable to use the general exchange equation in an equivalent and still general form

$$J_k = I_k^{\text{eq}} \left\{ \exp\left(-\sum_i v_{ik}^* (F_i^f - F_i^{\text{eq}}) / R\right) - \exp\left(-\sum_i v_{ik}^* (F_i^b - F_i^{\text{eq}}) / R\right) \right\}, \quad (29)$$

where

$$I_k^{\text{eq}} \equiv I_k^0 \exp(-v_{ik}^* F_i^{\text{eq}} / R) \quad (30)$$

is the common value of both absolute currents at equilibrium. The first derivatives of the net flux with respect to equilibrium potentials vanish

$$\frac{dJ_k}{dF_i^{\text{eq}}} = (I_k^{\text{eq}} v_{ik}^* R^{-1} + \frac{\partial I_k^{\text{eq}}}{\partial F_i^{\text{eq}}}) J_k / I_k^{\text{eq}} = (v_{ik}^* R^{-1} + \frac{\partial \ln I_k^{\text{eq}}}{\partial F_i^{\text{eq}}}) J_k = (v_{ik}^* R^{-1} - v_{ik}^* R^{-1}) J_k = 0 \quad (31)$$

For small deviations of potentials F_k from equilibrium and for small $\Delta F_k / R$, restricted to the first order small terms, Taylor expansion yields

$$J_i = I_i^{\text{eq}} \left\{ \sum_k v_{ki}^* (F_k^b - F_k^{\text{eq}}) / R - \sum_i v_{ki}^* (F_k^f - F_k^{\text{eq}}) / R \right\} = I_i^{\text{eq}} \left\{ \sum_k v_{ki}^* (F_k^b - F_k^f) / R \right\} = \sum_k L_{ik}^{\text{eq}} (F_k^b - F_k^f) \quad (32)$$

where $L_{ik}^{\text{eq}} \equiv I_i^{\text{eq}} v_{ki}^* / R$ is the Onsager's matrix at equilibrium. The general equality

$I_i^{\text{eq}} v_{ki}^* = I_k^{\text{eq}} v_{ik}^*$, discussed earlier, can be used to preserve Onsager's symmetry close to equilibrium. On the reverse, as the Onsager's symmetry is experimentally confirmed, it can constitute an argument for the validity of equality $I_i^{\text{eq}} v_{ki}^* = I_k^{\text{eq}} v_{ik}^*$ and general symmetry (26) within the present theoretical framework.

The expansion of the net flux in the Taylor series can be given an alternative form that uses the process affinity

$$J_i \cong \sum_k \{ I_i^{\text{eq}} v_{ki}^* (F_k^b - F_k^f) / R \} = I_i^{\text{eq}} A_i^s / R \quad (33)$$

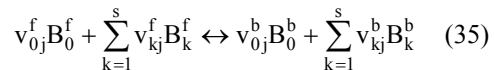
Thus, in the equilibrium vicinity the rate of each exchange process is proportional to its own affinity. This means that the frame of affinities is the frame of particular forces where the coefficients are diagonal, $\text{diag } L_{ik}^{\text{eq}} = (I_i^{\text{eq}} / R)$. The Onsager's form for the net kinetic current

$$J_i \cong \sum_k L_{ik}^{\text{eq}} (F_k^b - F_k^f) \quad (34)$$

($L_{ik}^{\text{eq}} \equiv I_i^{\text{eq}} v_{ki}^* / R$) is equivalent in an arbitrary frame to the affinity form on the basis of the general symmetry condition satisfied by all nonlinear equations of thermokinetics. The affinity form (33) and Onsager's form (34) constitute two equivalent complementary forms of linear equations of coupled exchange processes close to equilibrium.

5. Properties of Generalized Chemical Kinetics

Consider now the system of generalized chemical reactions



involving the energy B_0 ($k=0$) and chemical components B_k ($k=1, \dots, s$) that proceed at the rates r_1, \dots, r_N . This is the way to include heat effects in the formal description. Again we take into consideration of competition of forward and backward processes. Interestingly, the genuine chemical equilibrium is satisfied in a different way in this formalism than the equilibrium of exchange processes. As in the genuine chemical case the (unidirectional) stoichiometric coefficients are unequal, the chemical analogue of the expression (19) must be satisfied in both directions with different stoichiometric coefficients. This yields the equality

$$r_{j(f,b)}^{\text{eq}} \equiv r_j^0 \exp\left(-\sum_k v_{kj}^f F_k^{\text{eq}} / R\right) = I_j^0 \exp\left(-\sum_k v_{kj}^b F_k^{\text{eq}} / R\right) \quad (36)$$

for each reaction j . Clearly, for the vanishing rate,

this equality yields the classical condition of chemical equilibrium in the form

$$\exp\left\{\sum_k (v_{kj}^b - v_{kj}^f) F_k^{\text{eq}} / R\right\} = \exp(A_j^{\text{seq}} / R) = 1 \quad (37)$$

Consequently, as opposed to transport processes, absolute stoichiometric coefficients in genuine chemical reactions are unequal, whereas potentials F_k on both sides of the energy barrier in the kinetic regime are equal. The inequality of stoichiometric coefficients in states b and f ensures non-vanishing resulting coefficient v_{jk} and makes the chemical equilibrium unique.

For j-th elementary chemical step in f direction the kinetic formula is:

$$r_j^f = r_j^0 \exp\left(-\sum_k v_{kj}^f F_k^f / R\right) \quad (38)$$

With appropriate indices the same is valid for the backward reaction. The reaction rate is the net result of two opposite rates. At the chemical equilibrium both absolute rates equalize corresponding with the vanishing affinity as discussed above. The quantities r_j^0 ("exchange currents") are common for both directions. The net reaction rate corresponding with (38) is

$$J_j = r_j^0 \left\{ \exp\left(-\sum_k v_{kj}^f F_k^f / R\right) - \exp\left(-\sum_k v_{kj}^b F_k^b / R\right) \right\} \quad (39)$$

Whenever transports are fast, potentials F_i are equal at states f and b. If the transports are not fast, equations of the previous section should accompany the (non-simplified) equations of chemical kinetics with potentials F_i different at states f and b.

As the total number of the system coordinates s comprises the energy ($s=0$) and n components, the extended affinity of the entropy representation can be written in the form:

$$\begin{aligned} A_j^s &= \sum_{i=0}^s (v_{ij}^b F_i^b - v_{ij}^f F_i^f) \\ &= \sum_{i=1}^n \left(\frac{v_{ij}^f \mu_i^f}{T^f} \right) - \frac{v_{0j}^f}{T^f} - \sum_{i=1}^n \left(\frac{v_{ij}^b \mu_i^b}{T^b} \right) + \frac{v_{0j}^b}{T^b} \quad (40) \\ &= \Pi_j^f - \Pi_j^b \end{aligned}$$

In this equation generalized potentials Π_j of states f and b appear; they are defined as:

$$\Pi_j^f \equiv \sum_{i=1}^n \left(\frac{v_{ij}^f \mu_i^f}{T^f} \right) - \frac{v_{0j}^f}{T^f} \quad (41)$$

and

$$\Pi_j^b \equiv \sum_{i=1}^n \left(\frac{v_{ij}^b \mu_i^b}{T^b} \right) - \frac{v_{0j}^b}{T^b} \quad (42)$$

The potentials Π_j at states f and b are, respectively, unidirectional components of the extended affinity for reactants and products. When the classical part of the chemical reaction (governed by chemical potentials) is ignored the remaining term $\Delta \Pi_{\text{therm}}$ describes heat effects through the energy barrier, thus comprising the isothermal heat of reaction (at T^b , say) and the heat exchange:

$$\begin{aligned} (\Pi_j^f - \Pi_j^b)_{\text{therm}} &= \frac{v_{0j}^b}{T^b} - \frac{v_{0j}^f}{T^f} \\ &= \frac{v_{0j}^b - v_{0j}^f}{T^b} + \frac{v_{0j}^f (T^f - T^b)}{T^b T^f}. \end{aligned} \quad (43)$$

According to equation (38) in terms of Π_j the law of chemical kinetics for j-th elementary chemical step in f direction acquires the general structure

$$r_j^f = r_j^0 \exp(\Pi_j^f / R) \quad (44)$$

Consequently, an equation for the resulting rate of generalised rate process can be written as:

$$J_j = r_j^0 \left(\exp(\Pi_j^f / R) - \exp(\Pi_j^b / R) \right) \quad (45)$$

Thus, the f and b components of the extended affinity, Π_j^f and Π_j^b , play the same role in the chemical reaction kinetics as the temperature does in the heat exchange. In other words, Π_j^f and Π_j^b constitute potentials of the reaction because the j-th chemical reaction proceeds in the direction from a higher Π_j^f to a lower Π_j^b . Interestingly both Π_j^f and Π_j^b are state functions, so the reaction flow occurs from a higher to a lower Π in a similar way as the heat flow from a higher to a lower T . As the generalized expression for the forward potential Π_j^f (and the analogous expression for Π_j^b) shows

$$\Pi_j^f \equiv \sum_{i=1}^n (v_{ij} \mu_i T^{-1} - v_{0j} T^{-1})^f \quad (46)$$

the classical counterparts of Π_j^f and Π_j^b involving chemical potentials exclusively can yield rigorous chemical forces $\Pi_j^f - \Pi_j^b$ only in the case of isothermal conditions (isothermal energy barrier).

If reactions are independent, then the cross symmetry, understood as the equality of the derivatives of rates r_i with respect to potential Π_j , is satisfied trivially.

$$\frac{\partial r_j^f}{\partial \Pi_i} = \frac{\partial r_i^f}{\partial \Pi_j} = 0 \quad (47)$$

If the rank of stoichiometric matrices v_{ik}^f and v_{ik}^b is $Q < N$, the complete set of reactions (35)

will be linearly dependent and the maximum number of linearly independent chemical reactions will be Q . Let the set of generalized reactions ($u=1, 2, \dots, Q$)

$$\sum_{k=0}^s v_{ku}^f B_k^f \leftrightarrow \sum_{k=0}^s v_{ku}^b B_k^b \quad (48)$$

be such an independent subset. In this case the relations

$$\Pi_j^f \equiv \sum_{u=1}^Q \gamma_{ju} \Pi_u^f \quad \Pi_j^b \equiv \sum_{u=1}^Q \gamma_{ju} \Pi_u^b \quad (49)$$

and

$$r_u^{*f} \equiv \sum_{j=1}^N \gamma_{ju} r_j^f \quad r_u^{*b} \equiv \sum_{j=1}^N \gamma_{ju} r_j^b \quad (50)$$

hold for $u=1, 2, \dots, Q$. The coefficients γ_{ju} are small integers or zero. Substituting into the new (asterisk marked) rates, the expression $r_j^f = r_j^0 \exp(\Pi_j^f / R)$ of kinetic formula (44) and the linear expression $\Pi_j^f \equiv \sum_{u=1}^Q \gamma_{ju} \Pi_u^f$, we obtain for u -th reaction

$$r_u^{*f} \equiv \sum_{j=1}^N \gamma_{ju} r_j^f = \sum_{j=1}^N \gamma_{ju} r_j^0 \exp\left(\sum_{v=1}^Q \gamma_{jv} \Pi_v^f / R\right) \quad (51)$$

or, for w -th reaction

$$r_w^{*f} \equiv \sum_{j=1}^N \gamma_{jw} r_j^f = \sum_{j=1}^N \gamma_{jw} r_j^0 \exp\left(\sum_{v=1}^Q \gamma_{jv} \Pi_v^f / R\right) \quad (52)$$

($u, w = 1, 2, \dots, Q$). The cross equality of the derivatives of independent rates with respect to potentials Π_j is satisfied in a nontrivial way:

$$\frac{\partial r_u^{*f}}{\partial \Pi_w} = R^{-1} \sum_{j=1}^N \gamma_{ju} \gamma_{jw} r_j^0 \exp\left(\sum_{v=1}^Q \gamma_{jv} \Pi_v^f / R\right) = \frac{\partial r_w^{*f}}{\partial \Pi_u} \quad (53)$$

For more details see references (Lengyel and Gyarmati, 1981; Lengyel, 1992). Taking into account the basic expression for the absolute chemical rates

$$r_j^f = r_j^0 \exp\left(-\sum_k v_{kj}^f F_k^f / R\right) \quad (38)$$

and the general symmetry presupposed by Li in 1958

$$\frac{\partial r_j^f}{\partial F_k} = \frac{\partial r_k^f}{\partial F_j} \quad (54)$$

one could write down the following constraint on absolute rates k and j

$$\frac{\partial r_j^f}{\partial F_k} = -r_j^f v_{kj}^f / R = -r_k^f v_{jk}^f / R = \frac{\partial r_k^f}{\partial F_j} \quad (55)$$

and also analogous equalities for the backward reaction, b . Note the difference of these symmetries with well-known Onsager (1931)

symmetries that refer to derivatives of resulting rates or fluxes with respect to driving forces, \mathbf{X} , not the potentials \mathbf{F} .

6. Coupled Heat and Mass Exchange in Discontinuous Systems

Applying the present model of nonlinear macrokinetics, the coupled transfer of mass (m) and heat (h) is considered. This process is described by the general exchange equation

$$J_i = I_i^0 \left\{ \exp\left(-\sum_k v_{ki}^* F_k^f / R\right) - \exp\left(-\sum_k v_{ki}^* F_k^b / R\right) \right\} \quad (56)$$

whose equivalent form is

$$J_i = I_i^{\text{eq}} \left\{ \exp\left(-\sum_k v_{ki}^* (F_k^f - F_k^{\text{eq}}) / R\right) - \exp\left(-\sum_k v_{ki}^* (F_k^b - F_k^{\text{eq}}) / R\right) \right\} \quad (57)$$

with

$$I_i^{\text{eq}} \equiv I_i^0 \exp\left(-\sum_k v_{ki}^* F_k^{\text{eq}} / R\right) \quad (58)$$

as the common value of the absolute current at equilibrium.

The corresponding kinetic set contains two equations. The first one describes the mass flux of an active component (e.g., moisture)

$$J_1 = I_1^0 \left\{ \exp\left[v_{11}^* \left(\frac{\mu_m}{RT}\right)^f + v_{21}^* \left(-\frac{1}{RT}\right)^f\right] - \exp\left[v_{11}^* \left(\frac{\mu_m}{RT}\right)^b + v_{21}^* \left(-\frac{1}{RT}\right)^b\right] \right\} \quad (59)$$

and the second one- the heat flux $q=I_2$

$$J_2 = I_2^0 \left\{ \exp\left[v_{12}^* \left(\frac{\mu_m}{RT}\right)^f + v_{22}^* \left(-\frac{1}{RT}\right)^f\right] - \exp\left[v_{12}^* \left(\frac{\mu_m}{RT}\right)^b + v_{22}^* \left(-\frac{1}{RT}\right)^b\right] \right\} \quad (60)$$

Conditions that must be satisfied in order to assure the Onsager symmetries in the above kinetic equations are determined. Applying the formula (57) and expanding both kinetic expressions in the Taylor series subject to the assumption that the deviations of potentials F_i from F_i^{eq} are small (which means small driving forces), obtained is:

$$J_1 = I_1^{\text{eq}} \left\{ v_{11}^* \left[\left(\frac{\mu_m}{RT}\right)^f - \left(\frac{\mu_m}{RT}\right)^b \right] + v_{21}^* \left[\left(-\frac{1}{RT}\right)^f - \left(-\frac{1}{RT}\right)^b \right] \right\} \quad (61)$$

and

$$J_2 = I_2^{\text{eq}} \left\{ v_{12}^* \left[\left(\frac{\mu_m}{RT} \right)^f - \left(\frac{\mu_m}{RT} \right)^b \right] + v_{22}^* \left[\left(-\frac{1}{RT} \right)^f - \left(-\frac{1}{RT} \right)^b \right] \right\} \quad (62)$$

The equilibrium fluxes are defined in equation (58) above. The Onsager's matrix of this model is

$$L_{ik}^{\text{eq}} \equiv I_i^0 \exp(-v_{ki}^* F_k^{\text{eq}} / R) v_{ki}^* / R = I_i^{\text{eq}} v_{ki}^* / R \quad (63)$$

These equations prove that for an occasionally symmetric matrix v_{ki}^* , both absolute equilibrium currents I_1^{eq} and I_2^{eq} must be identical, so they must be replaced by a certain universal constant, I^{eq} . If, however, as usual, the discussed matrix is not symmetric, then the requirement of Onsagerian symmetries imposes appropriate connections between the currents I_1^{eq} and I_2^{eq} ; namely, $L_{12}^{\text{eq}} = I_1^{\text{eq}} v_{12}^* / R = I_2^{\text{eq}} v_{21}^* / R = L_{21}^{\text{eq}}$.

7. Coupled Thermal Fields

The concept of the energy barrier contains a restrictive ingredient caused by its discrete nature: it is not capable of avoiding mean quantities characteristic of the whole barrier, connected with finite affinities or driving forces. To describe the state transformation as a motion through the energy barrier treated as a continuum, an effort can be made to replace a logarithmic resistance governing linear systems (a mean quantity associated with a finite affinity) by its local counterpart. The result is a continuous description governed by a principle of the Fermat type with an infinite number of infinitesimal refractions of the ray (Sieniutycz, 2003). The results show that the path of chemical complex bends into a direction that ensures its shape associated with the longest residence time in regions of lower resistance, a property that makes it possible to predict shapes of chemical paths. (See Figure 4.)

The field counterpart of the theory implies that the diffusion coefficients D are not constants but are exponential functions of intensive state coordinates (temperature reciprocal and Planck potentials). The exponential dependence of D on $1/T$ was confirmed in a large number of experiments, especially in those describing diffusion in metals and melts and drying of solids.

For the thermal conduction process coupled with mass diffusion, a formula is obtained which is nonlinear with respect to the complete state vector \mathbf{C}

$$\mathbf{J}_q = L_{11}(\mathbf{C}) \mathbf{grad}(-T^{-1}) + L_{12}(\mathbf{C}) \mathbf{grad}(\mu T^{-1}) \quad (64)$$

Where L_{11} is the Onsager's thermal

conductivity connected with the usual one by the relation $L_{11} = \lambda T^2$. Besides concentrations c_k , vector \mathbf{C} may include energy density or T . The equation of this sort holds also for the mass flux \mathbf{J}_m .

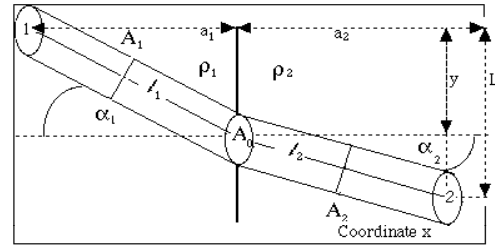


Figure 4. Illustration of Fermat-type principle for transport and rate processes. The motion is between two regions with different specific resistances ρ_1 and ρ_2 . The path in the coordinates x and y highlights "a ray". The area A_0 tangent to the surface separating two regions of constant ρ is a system constant. Yet, the areas $A_i = A_0 \cos \alpha_i$ ($i=1, 2$) perpendicular to the chemical flux decrease with angle α_i . The ray bends into a direction that ensures its shape associated with the longest residence time in regions of lowest resistance.

As the result of the integration along the gradient direction of the vector relationship

$$\mathbf{J}_j = -\lambda_j \mathbf{grad} \Pi_j \equiv \lambda_j \mathbf{grad} \left\{ \sum_{i=1}^n (Q_{ij} F_i) \right\} \quad (65)$$

a chemical Ohm's law follows in the form $\mathbf{J}_j = \Lambda_j A_j$. The integration of (65) is in the limits between $Q_{ij}^f = -v_{ij}^f / R$ and $Q_{ij}^b = -v_{ij}^b / R$. Replacing the usual scalar rate r_i by a vector chemical rate \mathbf{J}_i , such that $\mathbf{J}_i = r_i$, is operative in the physical space. This approach also includes electrochemistry whenever F_i is related to electrochemical potentials.

It may be shown that the general expression for the equilibrium Onsager's matrix of the related discrete model in terms of the pseudo-stoichiometric coefficients is

$$L_{ik}^{\text{eq}} \equiv I_i^0 \exp(-v_{ki}^* F_k^{\text{eq}} / R) v_{ki}^* / R = I_i^{\text{eq}} v_{ki}^* / R \quad (66)$$

8. Concluding Remarks

- In comparison with earlier approaches (Olah, 1997a,b; Lengyel and Gyarmati, 1981; Sieniutycz, 2004) the present formalism has the virtue of greater consistency and simplicity due to its direct relation to the tensor representation of the involved physical quantities in affine spaces. With the formalism, kinetics of typical macroscopic processes with exchange of energy

and matter can effectively be described by methods known for chemical reactions.

- Generalized kinetic equations for exchange processes and chemical reactions are of similar structure. Yet, absolute (unidirectional) stoichiometric coefficients for forward and backward steps are equal in transport processes whereas they are not in chemical reactions. In all cases Onsager's symmetries impose appropriate connections between absolute equilibrium currents.

- Only in close vicinity to the thermodynamic equilibrium rates of exchange processes or chemical reactions defined uniquely in terms of their affinities. The affinity picture - new for transport processes - and the traditional Onsagerian picture constitute two equivalent representations for the process kinetics. In the affinity picture both near and far from the thermodynamic equilibrium, the conductance matrix \mathbf{L} is diagonal and each flux is proportional to its own affinity. Yet, far from the equilibrium both the conductance matrix and kinetics depend on all state coordinates of the system.

- The distinction between kinetics expressed in terms of "difference of functions" and "functions of differences", equations. (20) and (21) respectively, should be underlined. This difference is useful to explain the violation of uniformity of optimal driving forces in nonlinear problems of finite time thermodynamics (Badescu, 2004). It may be shown that the optimal affinity profiles can be constant along the optimal paths only in the case of unconstrained problems with kinetics governed by the "functions of differences".

- The field counterpart of the theory implies that the diffusion coefficients D are not constants but are exponential functions of intensive state coordinates (temperature reciprocal and Planck potentials). The exponential dependence of D on $1/T$ was confirmed in a large number of experiments, especially in those describing diffusion in metals and melts and drying of solids (Olek et al., 2003).

- Affinity frames have not yet been used for transport processes; in view of their interesting properties further investigations seem reasonable along this research line. A promising feature refers to simultaneous studies of invariance properties in chemical and transport processes (Gorban et al., 1994) that should be studied more easily in affinity frames than in the frames using traditional driving forces.

- Generalizations of the theory are still possible to include finite propagation speeds. In particular, a simple method developed by Shter

(1973) for a traditional description of coupled transport phenomena can be used.

Acknowledgments

The author acknowledges the financial support from the Polish Committee of National Research (KBN); grant T09C 024 26 Non-equilibrium thermodynamics and optimization of chemical reactions in physical and biological systems.

Nomenclature

\mathcal{A}^s	vector of chemical affinities \mathbf{A}_j^s (entropy representation)
A_j	affinity of chemical reaction or a phase change
$a_i(c_i)$	activity of i -th component in terms of its concentration c_i
B_k	species participating in chemical reaction or transport process
\mathbf{C}	generalized state vector including energy in non-isothermal process
E	total energy density in a reaction-diffusion process
F_i	Gibbs potentials as partial derivatives of entropy with respect to extensive variables
\mathbf{I}^f	absolute (unidirectional) flux vector in the forward direction
I_k^b	backward flux of k -th species in a transport process
I_k^f	forward flux of k -th species in a transport process
\mathbf{J}_k	resulting vector of flux density of species k in a transport process
J_{el}	density of electric current (Section 2)
J_j	resulting density of chemical flux of j -th reaction
$K=k^f/k^b$	chemical equilibrium constant
L_{ik}	Onsager's phenomenological coefficients
N	n , number of reactions and number of species, respectively
q	heat flux
R	universal gas constant
r_j	volumetric rate of j -th reaction
S	entropy density in a reaction-diffusion process
S_σ	entropy production
S	number of state coordinates in the generalized system
T	temperature
t	time
V	volume
\mathbf{X}	vector of classical thermodynamic forces

Greek Symbols

v_{ij}	stoichiometric matrix of j -th reaction
----------	---

V_{ik}^*	peculiar stoichiometric matrix for a coupled transport process
μ_i	molar chemical potential of i -th component
Π^f, Π^b	substrate and product part of chemical affinity

Subscripts

i, k	i th and k th components
j	Elementary reaction number
m	Mass
0	Energy as zero-th component
q	Sensible heat

Superscripts

B	backward direction
Eq	thermodynamic equilibrium
F	forward direction
Net	resulting value
0	exchange current
s	entropy representation
$*$	peculiar quantity

References

- Badescu, V., 2004, Optimal paths for minimizing lost available work during usual heat transfer processes, *J. Non-Equilib. Thermodyn.*, 29, 53-73.
- Bockriss, J. O'M., Drazic, D.M., 1972, *Electrochemical Science*, Taylor and Francis, London.
- Callen, H. B., 1985, *Thermodynamics and Introduction to Thermostatistics*, 2nd ed., Wiley, New York.
- Glasstone, S., Laidler, K., Eyring H., 1941, *The Theory of Rate Processes*, McGraw-Hill, New York.
- Gorban, A. N., Karlin, I. V., Zinovyev, A. Yu., 2004, Invariant grids for reaction kinetics, *Physica A* 333, 106-154.
- Guldberg, C. M., Waage, P., 1867, *Etudes Sur Les Affinités Chimiques*, Brogger and Christie, Christiania.
- Keizer, J., 1987, *Statistical Thermodynamics of Nonequilibrium Processes*, Springer, New York.
- Lengyel, S., 1988, Deduction of the Guldberg-Waage Mass Action Law from Gyarmati's Governing Principle of Dissipative Processes, *J. Chem. Phys.* 88, 1617-1621.
- Lengyel, S., 1992, Consistency of chemical kinetics with thermodynamics. Article in: *Flow, Diffusion and Transport Processes, Advances in Thermodyn.* 6: 283-302.

Lengyel, S., Gyarmati, I., 1981, On the thermodynamics of elementary chemical reactions in homogeneous systems, *J. Chem. Phys.* 75, 2384-2389.

Lengyel, S., Gyarmati, I., 1986, Constitutive equations and reciprocity relations of nonideal homogeneous closed chemical systems, *Acta Chem. Hung.* 122, 7-17.

Li, C. M., 1958, Thermodynamics of nonisothermal systems. The classical formulation. *J. Chem. Phys.* 29, 747-754.

Oláh, K., 1997a, The way to thermokinetics, *ACH-Models in Chemistry* 134, 343-367.

Oláh, K., 1997b, Electrode thermokinetics, *Periodica Polytechnica Chem.Eng.* 41, 97-114.

Oláh, K., 1998, Reciprocity relations: Maxwell, Onsager, a thermokinetic approach, *Periodica Polytechnica Chem. Eng.* 42, 21-32.

Olek, W., Perre, P., Weres, J., 2003, Computer-aided identification of bound water diffusion coefficient in wood, *Proceedings of X Symposium Suszarnictwa, Łódź*, 17-19 September 2003, pp. 769-777.

Onsager, L., 1931, Reciprocal relations in irreversible processes, I. *Phys. Rev.* 37, 405, 1931; II. *Phys. Rev.* 38, 2265.

Prigogine, I., 1959, *Thermodynamics of Irreversible Processes*, Interscience, New York.

Shiner, J.S., 1987, Algebraic symmetry in chemical reaction systems at stationary states arbitrarily far from equilibrium, *J. Chem. Phys.* 87, 1089-1094 (1987).

Shter, I.M., 2004, The generalized Onsager principle and its application, *Inzh. Fiz. Zh.* 25, 736-742.

Sieniutycz, S., 1987, From a least action principle to mass action law and extended affinity, *Chem.Eng. Sci.* 42, 2697-2711.

Sieniutycz, S., 2003, Extremum properties of interphase chemical reactions in catalytic systems, *Catalysis Today* 79-80C, 307-313.

Sieniutycz, S., 2004, Nonlinear thermokinetics of heat & mass transfer and chemical or electrochemical reactions, *Intern.J. Heat & Mass Transfer*, 47, 515-526.

Waldram, J. R., 1984, *The Theory of Thermodynamics*, pp. 22-24, Cambridge University Press, Cambridge, See also Tolman, R. C., 1924, *Phys. Rev.* 23, 699, (1924).