Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

International Journal of Heat and Mass Transfer 47 (2004) 515–526

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Nonlinear macrokinetics of heat and mass transfer and chemical or electrochemical reactions ☆

Stanislaw Sieniutycz *

Faculty of Chemical and Process Engineering, Warsaw University of Technology, 1 Waryńskiego Street, 00-645 Warsaw, Poland

Received 4 July 2003

Dedicated to Prof. Karoly Oláh (Budapest University of Technology and Economics, Department of Chemical Physics)

Abstract

We consider single-phase and multiphase disequilibrium processes in presence of nonlinear heat and mass transfer as well as chemical or electrochemical reactions. An approach accepted distinguishes in each elementary process, diffusive or chemical, two competing (unidirectional) fluxes. They are equal in the state of thermodynamic equilibrium and their difference off equilibrium constitutes the observed resulting flux representing the rate of chemical reaction. We stress the role of nonlinear chemical (electrochemical) resistance and chemical (electrochemical) affinity. The nonequilibrium systems under investigation are described by equations of nonlinear kinetics of Marcelin–de Donder type containing exponential terms with respect to chemical potentials of Planck and temperature reciprocal, that simultaneously are analytical expressions characterizing the transport of the substance or energy by the energy barrier. We show how the kinetics of this sort follows from the law of mass action, what are its consequences closely and far from equilibrium, and also how a basic equation of chemical or electrochemical kinetics (Butler–Volmer) emerges. We also stress the significance of nonlinear chemical (electrochemical) resistance and of the chemical (electrochemical) affinity. Simultaneously we stress restrictiveness of the discrete energy barrier, which is not capable of avoiding mean quantities characteristic of the whole barrier and connected with finite affinities or driving forces.

To describe the chemical transformation as a motion through the energy barrier treated as a continuum an effort is made to replace the logarithmic chemical resistance (a mean quantity associated with a finite affinity) by its local counterpart. The result is a continuous description, governed by a principle of Fermat type with an infinite number of infinitesimal refractions of the ray. The results show that the path of chemical complex bends into a direction that ensures its shape associated with longest residence time in regions of lower resistivity. These properties make it possible to predict shapes of chemical paths.

Keywords: Nonlinear kinetics; Chemical Ohm's law; Electrochemical resistance

---

1. Introduction

In this work nonlinear kinetics are analyzed in systems that may react chemically (electrochemically) and may exhibit phase changes. The research method investigates phenomena of nonlinear diffusion, heat conduction, phase changes and chemical reactions in the context of nonlinear resistances, extended chemical affinity, theory called thermokinetics and variational principle of Fermat type.

The meaning of chemical reaction coordinate and the second law of thermodynamics are applied. Chemical Ohm's law, $r_j = A_j/R_j$, which defines the resulting rate of an elementary process, is transformed into a local form resembling the Fourier's law of heat conduction. In

---

☆ The paper is an extended and improved version of the talk presented at III Workshop "Modeling of multiphase flows in thermochemical systems", Stawiska near Kościerzyna, Poland 14–16.09.2003.

* Tel.: +48-22-825-6340; fax: +48-22-825-1440.

E-mail address: sieniutycz@ichip.pw.edu.pl (S. Sieniutycz).

0017-9310/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0017-9310(03)00412-5

Nomenclature

A	area perpendicular to flow
A_0	constant area of a flux tube intercepted by the interface
$\mathbf{A}^s$	vector of chemical affinities A_j^s (entropy representation)
A	affinity of chemical reaction
$a_i(c_i)$	activity of ith component in terms of its concentration c_i
F_i	Gibbs potentials as partial derivatives of entropy with respect to extensive variables
I_j	chemical flux or the derivative dn_j/dt for jth reaction
J_j	density of chemical flux of jth reaction
k	reaction rate constant
l	length coordinate
N, n	number of reactions and number of species, respectively
P_j	production function of jth reaction
ξ_j	degree of advancement for jth reaction
q	heat flux
R	gas constant
R_j	standard volumetric resistance of jth reaction
$\mathscr{R}$	total chemical resistance of reaction
r_j	volumetric rate of jth reaction
S, S_σ	entropy and entropy production, respectively
T	temperature
t	time
u	controlled slope dy/dx, local direction of gradient of Π
V	volume, potential
W	moisture
x	dryness content in boiling example
x, y	horizontal and vertical coordinate, respectively

Greek symbols

α	incidence angle between the gradient of Π and normal to plane of constant ρ
ρ_j	specific chemical resistance of jth elementary reaction
ν_{ij}	stoichiometric matrix of jth reaction ($\nu_{ij} \equiv \nu_{ij}^b - \nu_{ij}^f$)
Φ_σ, Ψ_σ	rate dependent and state dependent dissipation function, respectively
μ_i	molar chemical potential of ith component
Π^f, Π^b	substrate and product part of chemical affinity

Subscripts

i	ith component
j	elementary reaction number
m	minimum
σ	dissipative property

Superscripts

b	backward
f	forward
s	entropy representation

this local form the role of temperature is played by the unidirectional component of chemical affinity whereas the role of heat conductivity is played by the reciprocal of specific chemical resistance. This form makes it possible to formulate the problem of an optimal shape for a "chemical ray" in the physical space by solving a corresponding variational problem. The problem represents a continuous variant of the chemical Fermat principle with an infinite number of infinitesimal refractions of the ray, similar to the *continuous* version the Fermat principle in a optically inhomogeneous medium.

For the fluxes of heat mass and chemical flux, a "law of bending" is determined in suitable reference frames which implies that—by minimizing the total resistance—the chemical ray spanned between two given points takes the shape assuring its relatively large part in a region of lower chemical resistivity (a 'rarer' region of the medium). In effect, the chemical flux bends into the direction that ensures its shape consistent with the longest residence of a definite charge (of mass, energy or chemical complex) in regions of lowered resistivity.

To increase simplicity and lucidity of its interpretation, the principle of path bending is formulated in some particular frame of coordinates x and y in which the local resistance for the flow of a stream (of substance or heat) changes as a function of a distinguished coordinate x; the coordinate y is then tangent to the surface of the constant specific resistance $\rho = C$. In the analysis of the problem essential role is played by the slope coefficient $u = dy/dx$ that describes the local direction of the gradient of an appropriate potential (temperature reciprocal, Planck potential, etc.).

Methods of dynamic optimization (variational calculus, maximum principle and dynamic programming) are applied to quantitatively describe chemical or thermal flows as orthogonal (transversal) trajectories of corresponding "wavefronts" or surfaces of constant resistance $\rho = C$ (constant time in the typical Fermat problems).

2. Thermodynamics of multiphase systems

Let us first recall two basic approaches to thermodynamic modeling of multiphase systems.

In the first approach one assumes that in the investigated system all phases and interphase surfaces are known (or we are able to determine them), and, by this, within each phase and for each interface a separate analysis can be performed. Such an analysis uses for each phase methods stemming from thermodynamics of single-phase systems, and supplements the results obtained by those stemming from analyses of the phenomena occurring at interfaces. Examples of such approach are usually provided in earlier works [1–3].

Frequently, however, an extremely large number of phases is present in the system (e.g. in dispersed and boiling systems), and interfaces may vary in the process. The matter can also be complicated by phase transformations and surface reactions. The first approach is then fruitless.

In the second approach (generally more effective) it is assumed that the multiphase system constitutes an isotropic mixture that has definite operational properties, thermodynamic and transport. One deals then with the model of fluid with microstructure whose thermodynamic and transport properties are described by such operational quantities as: operational specific heat, operational first and second viscosity, operational heat conductivity, etc. Effectiveness of the approach based on operational quantities was recently shown in series of works on flow boiling and condensation, see, for example [4,5].

In the context of the variational approach, which may be applied whenever one knows a relevant functional and a variational principle, the idea of minimum entropy generation can be applied that was originally exploited in single-phase systems. We can illustrate the approach of this sort with example of the so-called *flashing*, i.e. boiling of expanding water in the nozzle, where intense evaporation occurs caused by a rapid pressure drop and the increase of the flow velocity [3].

In thermodynamic descriptions of multiphase, chemically reacting media important role is played by matrices R_{ik} and g_{ik}, that contain operational chemical resistances and conductances of transport processes. The matrix of chemical resistances $\mathscr{R}$ can be applied to describe both chemical reactions and phase changes. The state matrix $\mathbf{C} = (c_1, \ldots, c_n, c_e)$ is the vector composed of molar concentrations and energy density. The vector of potentials is represented by the column matrix $\mathbf{F}$ defined as

$$\mathbf{F} = (-\mu_1 T^{-1}, -\mu_2 T^{-1}, \ldots, -\mu_n T^{-1}, T^{-1})^{\mathrm{T}} \tag{1}$$

Classical definition of the chemical affinity [6] is here transferred to the entropy representation and extended so that it can take into account transport phenomena. Both the extension and its classical counterpart are shown in Eq. (2) below. In the case when transport processes are absent standard affinity is recovered as shown by the arrow in the equation below

$$A_j^{\mathrm{s}} = \sum_{i=1}^{n} (v_{ij}^{\mathrm{b}} F_i^{\mathrm{b}} - v_{ij}^{\mathrm{f}} F_i^{\mathrm{f}}) \to \sum_{i=1}^{n} v_{ij} F_i = (\mathbf{v}^{\mathrm{T}} \mathbf{F})_j \tag{2}$$

Entropy source in the system describes both transport and rate processes in terms of net rates r_j and differences in transfer potentials F_i. Matrix $\mathscr{R}$ defined by Eq. (3) below is a nonlinear generalized matrix of chemical resistances, so that its entries refer to the chemical dissipation and dissipation caused by accompanying transports. Vector $\mathbf{r}$ comprises the reaction rates and rates of transports, and, in the classical case, the product $\mathbf{v}^{\mathrm{T}}\,\mathbf{F}$ describes the traditional vector of chemical affinities in the entropy representation, A^{s}. Chemical resistances satisfy the logarithmic formula [7–10]

$$R_j(\mathbf{a}, T) = \mathsf{R} \ln \left[\left(k_j^{\mathrm{f}} \prod_{i=1}^{n} a_i^{v_{ij}^{\mathrm{f}}} \right) - \ln \left(k_j^{\mathrm{b}} \prod_{i=1}^{n} a_i^{v_{ij}^{\mathrm{b}}} \right) \right] \Bigg/ \left[k_j^{\mathrm{f}} \prod_{i=1}^{n} c_i^{v_{ij}^{\mathrm{f}}} - k_j^{\mathrm{b}} \prod_{i=1}^{n} a_i^{v_{ij}^{\mathrm{b}}} \right] \tag{3}$$

where a_i are activities. For systems close to ideal ones use of concentrations, c_i is sufficient.

3. Example of boiling as a chemical reaction

We discuss here an equation describing the kinetics of new phase creation (vapor) during flashing, that is, boiling of expanding water in a nozzle in which intense evaporation occurs caused by the large pressure drop and consistent increase of the velocity. Production of vapor in the flashing zone and its later disappearance in the "shock wave" are described by a relaxation–diffusion model [5].

Assuming that the disequilibrium caused by the creation of vapor bubbles is defined as the difference in the dryness fraction $x^{\mathrm{e}} - x$, the vapor production can be treated as a chemical reaction described by the resistance equation (a special case of the general resistance (3))

$$R(x) = \mathsf{R} \frac{\ln[k^{\mathrm{f}}(1-x)/(k^{\mathrm{b}} x)]}{k^{\mathrm{f}}(1-x) - k^{\mathrm{b}} x} \tag{4}$$

and by the chemical affinity of vapor creation (in entropy representation). In terms of the dryness fraction x, the increase of which per unit time $\mathrm{d}x/\mathrm{d}t$ represents the net rate of the vapor generation r, we obtain the affinity

$$A = (\mu/T)^{\mathrm{f}} - (\mu/T)^{\mathrm{b}} = \mathsf{R} \ln \left(\frac{r^{\mathrm{f}}}{r^{\mathrm{b}}} \right) \cong \mathsf{R} \ln[k^{\mathrm{f}}(1-x)/(k^{\mathrm{b}} x)] \tag{5}$$

The affinity of inverse process, i.e. condensation, equals $-A$. Then the chemical Ohm law

$$\frac{\mathrm{d}x}{\mathrm{d}t} = r^{\mathrm{f}} - r^{\mathrm{b}} = \frac{A}{R} \tag{6}$$

[7–10] implies the kinetic equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k^{\mathrm{f}}(1-x) - k^{\mathrm{b}}x \tag{7}$$

Equilibrium dryness fraction (for $r = 0$) satisfies the equation

$$k^{\mathrm{f}} = (k^{\mathrm{f}} + k^{\mathrm{b}})x_{\mathrm{e}} \tag{8}$$

so that the equilibrium dryness fraction of vapor is

$$x_{\mathrm{e}} = k^{\mathrm{f}}/(k^{\mathrm{f}} + k^{\mathrm{b}}) \tag{9}$$

After applying the equilibrium dryness fraction in Eq. (7) the kinetics of vapor generation becomes described by the equation

$$r = \frac{\mathrm{d}x}{\mathrm{d}t} = (k^{\mathrm{f}} + k^{\mathrm{b}})(x_{\mathrm{e}} - x) \tag{10}$$

This is, of course, a familiar relaxation equation with the transfer coefficient $K = k^{\mathrm{f}} + k^{\mathrm{b}}$ and relaxation time $\tau = K^{-1}$. This equation proves that the process of vapor production in the flashing regime may be described as a chemical reaction with the chemical affinity (5) and the chemical resistance (4).

Regarding experimental corraboration of Eq. (10) and determining of the relaxation time τ, see, for example, [5]. The discussed kinetics is in general neither isothermal nor isobaric because the rate constants k^{f} and k^{b} can be referred to two different temperatures that depend in a given instant on the process course. If the variables used to describe relaxation are, e.g., x, p and s, then the difference $x^{\mathrm{e}} - x$ may be presented as the linear combination of the differences $(x^{\mathrm{e}} - x)_{s,p}$, $(p^{\mathrm{e}} - p)_{s,x}$ and $(s^{\mathrm{e}} - s)_{p,x}$ multiplied by related coefficients. This is consistent with the general structure of the relaxation equations for processes of this sort [4,5].

The approach that applies resistance (3) in the particular form (4) provides therefore a way to describe the flashing process as interphase chemical reaction. In the regimes of flashing and condensation, i.e. where sources of new phase are important, the fluid model (which elsewhere may be that of an perfect fluid) is necessarily a model of a viscous fluid that conducts the heat. It is also the model of the fluid with microstructure, in fact, a new phase, where the transfer processes are described via operational coefficients of viscosity and heat conductivity. Yet, a true difficulty in this example consists in the derivation of a complete set of kinetic and balance equations, along with equations describing pressure, velocity field, and various modes of momentum transport. This, in fact, could be broken down to variational derivation of the equation of change for momentum (Navier–Stokes equation). Equations of motions are in this case inevitable if we do not want to distort our modeling far beyond an admissible accuracy.

4. Introduction to nonlinear models of thermokinetics

Below we discuss main problems of nonlinear disequilibrium systems focusing on applications to chemical or electrochemical processes and coupled heat and mass transfer. We concentrate our discussion on several general aspects of the nonlinear theory which are in direct connection with nonequilibrium thermodynamics and occasionally stress some other applications that may have a practical utility for various process techniques.

In particular, on the example of Marcelin–de Donder kinetic equations, we introduce a "thermokinetic analysis" and discuss its link with engineering descriptions of processes analyzed as single-phase- and pseudo-homogeneous multiphase systems. We next show that a critical analysis of the literature equations leads to amended structures that have secured the uniqueness of conditions describing chemical and thermodynamic equilibria and satisfy the Onsager's symmetries for small driving forces [11]. We point out that in the conventional description of irreversible processes considered are net fluxes and net thermodynamic forces (Fig. 1). Traditional rate equations and exchange equations are postulated as relationships of the following type

$$\mathbf{J} = f(\mathbf{X}) \quad \mathbf{J} \equiv -\Delta\mathbf{j}; \quad \mathbf{X} \equiv \Delta\mathbf{F}$$

In the Onsager theory $\mathbf{J}_i = \Sigma_k L_{ik}\mathbf{X}_k$, where L_{ik} is a respective phenomenological coefficient that has the meaning of a conductance. In many cases, especially for situations far from equilibrium this type of the rate formulas is not unique.

Thermokinetics is capable of describing nonlinear processes with the transport of energy and substance in the bulks of phases or at interfaces, the rates of these processes being described by models of chemical reactions. By analyzing two competing directions of an elementary process as a direct and reverse reaction thermodynamic disequilibrium systems are investigated that are described by generalized equations of Marcelin–de Donder type [12–17]. These equations contain expo-

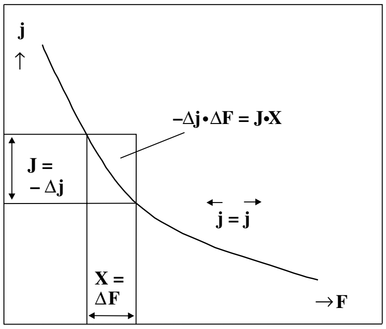

Fig. 1. Oláh's interpretation of net fluxes **J** and classical driving forces **X** (http://knight.kit.bme.hu/olah/olah-06.htm).

nential terms with Planck potentials and temperature reciprocal, and they simultaneously are analytical expressions characterizing the transfer of substance or energy through the energy barrier [18]. Similar equations were used by de Vos in his analysis of currents of photons and electrons in semiconductors as elements of solar cells [19].

As shown here and in some other sources, kinetics of this sort are consistent with the mass action law [20], and have far-reaching consequences to distinguish between processes close and far from the thermodynamic equilibrium. With these kinetics one can also determine thermodynamic and kinetic criteria for correctness of many approximate kinetic equations used in the literature. We stress a common for various systems methodology based on Gibbs equation and principles of thermodynamics of irreversible processes [6,21]).

A process of new phase creation, during evaporation for example, may be understood either as the usual phase change

$$W_g = W_l \tag{11}$$

or as a special chemical reaction (with the stoichiometric coefficient $v^f = 1$ for the substance in the liquid state and the coefficient $v^b = 1$ for this substance in the gaseous state). In this reaction the product is the mass (or mole number) transferred from the liquid to the gas, and the conversion degree is the quantity of the evaporated liquid per unit mass of the system. The driving force of such a chemical reaction is its ‘affinity’, $A = \mu_s - \mu_g$, or its nonisothermal generalization $A = \mu_s/T_s - \mu_g/T_g$.

Approximate kinetic models of linear irreversible thermodynamics hold true in the regime of linear proportionality between thermodynamic fluxes and forces. In this regime these models conform with the experimentally confirmed observation that in the regime close to equilibrium the reaction rate or the rate of phase change is proportional to the chemical affinity. This observation is sometimes applied in various process techniques, in approaches when the physical transformation (e.g. evaporation) is treated as a special reaction (as in the example discussed above). In the process thermodynamics a conclusion can then be formulated that knowledge of the affinity A suffices to predict the process rate. However, the use of the affinity A for the purpose of the unique determination of the rate is admissible only in a strictly linear regime located in close vicinity of the equilibrium manifold. This means that the results obtained with the help of linear models became too approximate (and hence unacceptable) in regimes of state changes where nonlinear properties are essential. In particular, the simple conclusion that allows to apply the affinity A as the single variable sufficient to describe the process rate is no longer valid. In fact, applicability of approximations based on linear models is often doubtful in the realm of experiments, both in chemical and physical kinetics. The need for a nonlinear theory is obvious when one wants to describe process rates in a more exact way.

5. Kinetics of Marcelin–de Donder

The Marcelin–de Donder kinetic scheme represents the first and already important example of the structure that appears in general equations of thermokinetics. This kinetic scheme represents a form of the kinetic mass action law in which chemical potentials appear instead concentrations. To derive the Marcelin–de Donder form of the kinetic law of mass action we consider the general chemical reaction

$$\sum_{i=1}^{n} v_{ij}^{f} A_i \leftrightarrow \sum_{i=1}^{n} v_{ij}^{b} A_i \quad i = 1, 2, \ldots, n \quad \text{and} \quad j = 1, 2, \ldots N \tag{12}$$

satisfying the classical mass action law in the form

$$r_j = r_j^f - r_j^b = k_j^f(T) \prod_{i=1}^{n} c_i^{v_{ij}^f} - k_j^b(T) \prod_{i=1}^{n} c_i^{v_{ij}^b} \tag{13}$$

Exploiting the usual structure of chemical potentials

$$\mu_i(c_i, T) = \mu_{i0}(T) + RT \ln c_i \tag{14}$$

the concentrations c_i can be obtained in the form

$$c_i = \exp\left(\frac{\mu_i}{RT}\right) \exp\left(-\frac{\mu_{i0}}{RT}\right) \tag{15}$$

Substituting Eq. (15) into (13) we obtain the rate equation in the Marcelin–de Donder form

$$\begin{aligned} r_j(\mathbf{c}, T) &= r_j^f(\mathbf{c}, T) - r_j^b(\mathbf{c}, T) \\ &= r_j^0(T)\left(\exp\sum_{i=1}^{n} v_{ij}^f \frac{\mu_i}{RT} - \exp\sum_{i=1}^{n} v_{ij}^b \frac{\mu_i}{RT}\right) \end{aligned} \tag{16}$$

that already has the typical (while still not the most general) structure of equations of thermokinetics. Its virtue is a single reaction rate constant, r_j^0, which represents the so-called *exchange current* (Its electrochemical counterpart is interpretted in Figs. 2 and 3.). Another virtue of this structure is explicit satisfaction of the detailed balance at the thermodynamic equilibrium. In ionic systems chemical potentials in the above equations should be replaced by electrochemical potentials. The exchange current expressed in terms of “usual” reaction rate constants has the form

$$\begin{aligned} r_j^0(T) &\equiv k_j^f(\mathbf{c}, T)\left(\exp\sum_{i=1}^{n} - v_{ij}^f \frac{\mu_{i0}}{RT}\right) \\ &= k_j^b(\mathbf{c}, T)\left(\exp\sum_{i=1}^{n} - v_{ij}^b \frac{\mu_{i0}}{RT}\right) \end{aligned} \tag{17}$$

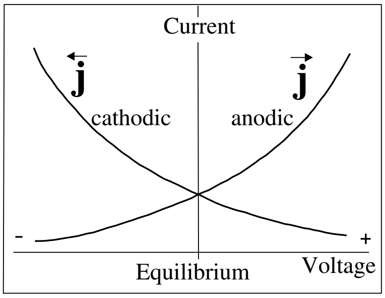

Fig. 2. Oláh's interpretation of anodic and cathodic currents as well as of the exchange current in terms of voltage. Abscissa of crossing point of both currents describes the exchange current.

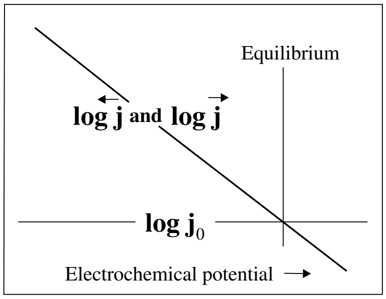

Fig. 3. Oláh's interpretation of logarithms of anodic and cathodic currents as well as of the exchange current in terms of electrochemical potential.

The quantity r_j^0 is well known in electrochemistry. We observe that it is just the condition of vanishing electrochemical affinity that implies the necessity of equality of both right hand sides of Eq. (17). More precisely, the common value of r_j^0 for the forward and backward reaction follows as the consequence of the fact that in order to assure the vanishing chemical (electrochemical) affinity at equilibrium both expressions in Eq. (17) must be equal at every instant of time. This allows to define the universal reaction rate constant r_j^0 or the exchange current in electrochemistry (Electrochemical rates are designated by the letter j rather than γ in Figs. 1–3.). Moreover, in order to treat electrochemical systems correctly, the chemical potentials in the above equations should be replaced by the electrochemical potentials.

The result is the Butler–Volmer equation that describes the electric current as difference of anodic and cathodic currents [22]. In terms of the electrochemical rather than chemical potentials (the former are designated by tildas) and the net electric current J as the difference between the anodic and cathodic currents the Butler–Volmer equation has the form

$$\begin{aligned} J &= j^{\text{anod}}(\mathbf{c},T) - j^{\text{cathod}}(\mathbf{c},T) \\ &= j^0(T)\left(\exp\sum_{i=1}^{n} \nu_i^{\rm f}\frac{\tilde{\mu}_i}{RT} - \exp\sum_{i=1}^{n} \nu_i^{\rm b}\frac{\tilde{\mu}_i}{RT}\right) \qquad (18) \end{aligned}$$

Popular, equivalent form of this equation describes the electric current of a cell in terms of the overvoltage η and Faraday constant F

$$J = j^0(\exp((1-\alpha)F\eta/RT) - \exp(-\alpha F\eta/RT)) \qquad (19)$$

[22]. In the literature more information on electrode thermokinetics can be found, see, for example [16,22].

According to Oláh [16] one may distinguish the three basic stages in the development of the theories of electrode processes. In the first step Tafel observed in 1905 that some electrochemical processes undergo at a substantially different voltage than it would be expected from thermodynamic calculations, i.e. the overpotential was discovered. In 1930 Erdey-Gruz and Volmer made a substantial progress in interpreting experiments. The theory developed by them can be regarded as the beginning of the modern thermokinetic theory used nowadays [15–17]). The basic statements of the contemporary interpretation are: (a) The current measured by the ammeter in series with the cell is actually a "net" current, or the difference of two opposite "absolute" currents (the anodic current and the cathodic current); (b) At equilibrium the absolute unidirectional currents equalize but do not vanish; they define the "exchange currents"; (c) The absolute currents are exponential functions of the voltage; (d.) The voltage-dependences of the anodic and cathodic currents, differ one from another. This is presented in a lucid way in Oláh graphs that may be found on his website: http://knight.kit.bme.hu/olah/olah-10.htm/.

6. General equations of nonlinear thermokinetics

We shall now discuss generalizations of the above kinetic schemes. The general equations of thermokinetics are formulated for a set of chemical reactions, $j = 1, 2, \ldots, N$

$$\sum_{i=1}^{n} \nu_{ij}^{\rm f} A_i^{\rm f} \leftrightarrow \sum_{i=1}^{n} \nu_{ij}^{\rm b} A_i^{\rm b} \qquad (20)$$

between the species $i = 1, 2, \ldots, n$ and also for the transport (diffusion) processes involving the same species. Both groups of processes are described by in principle the same basic equations of nonlinear thermokinetics; the differences appear when stoichiometric coefficients are treated, which are equal on both sides of the energy barrier in the case of transport processes.

For an undirectional elementary process in the forward direction

$$r_j^{\rm f} = r_j^0 \exp\left(-\sum_i \nu_{ji}^{\rm f} F_i^{\rm f}\right) \quad j = 1, 2, \ldots, N \qquad (21)$$

and the same structure holds for the backward process with only the difference in indices. As there are two competing processes, direct and reverse (or forward and backward), the net process rate is

$$r_j = r_j^{\mathrm{f}} - r_j^{\mathrm{b}} = r_j^0\left(\exp\left(-\sum_i \nu_{ji}^{\mathrm{f}} F_i^{\mathrm{f}}\right) - \exp\left(-\sum_i \nu_{ji}^{\mathrm{b}} F_i^{\mathrm{b}}\right)\right) \tag{22}$$

In these equations F_i are the potentials $(1/T, -\mu_i/T)$ or the partial derivatives of the entropy with respect to the extensive quantities in the Gibbs equation. In the kinetic regime (fast transports, $F_i^{\mathrm{f}} = F_i^{\mathrm{b}} = F_i^{\mathrm{eq}}$) one recovers the classical chemical kinetics in the Marcelin–de Donder form (16), whereas in the diffusion-controlled regime (fast reactions) the process behalves in accordance with the laws of nonlinear diffusion.

Eq. (23) below, based on (22), makes it possible to treat the diffusion of the energy and components, thus, it represents a generalization of the isothermal kinetics of the Marcelin–de Donder (16). The generalized formula (23) is no longer restricted to the kinetic regime as its original counterpart (16)

$$r_j(\mathbf{c}, T) = r_j^0(T)\left(\exp\sum_{i=0}^{n} \nu_{ij}^{\mathrm{f}} \frac{\mu_i^{\mathrm{f}}}{\mathrm{R}T^{\mathrm{f}}} - \exp\sum_{i=0}^{n} \nu_{ij}^{\mathrm{b}} \frac{\mu_i^{\mathrm{b}}}{\mathrm{R}T^{\mathrm{b}}}\right) \tag{23}$$

($\mu_i \equiv 1$ for $i = 0$, corresponding with the energy transfer.) The general relationship (22) is thus capable of including slow transport processes and nonisothermal effects. Due to the presence of the potentials of the same component in both terms of Eq. (23), which means the component presence at both sides of the barrier, autocatalytic effects can be investigated.

In the considerations that follow we use the nondimensional affinities of the entropy representation, A_j. For an isothermal energy barrier these are connected with the classical affinities by the equation

$$A_j \equiv A_j^{\mathrm{class}}/(\mathrm{R}T) \tag{24}$$

The stoichiometric coefficients satisfy the constraint resulting from the mass conservation law in each chemical reaction

$$\sum_i (\nu_{ji}^{\mathrm{b}} - \nu_{ji}^{\mathrm{f}}) M_i = \sum_i \nu_{ji} M_i = 0 \tag{25}$$

In the case of elementary transport processes, the general reacting scheme (20) assumes a simple form. Namely, for each *i*th transported component separately

$$\nu_i^{\mathrm{f}} B_i^{\mathrm{f}} \leftrightarrow \nu_i^{\mathrm{b}} B_i^{\mathrm{b}} \quad i = 1, 2, \ldots, n \tag{26}$$

However a more general form with ν_{ki} can also emerge, associated with Onsagerian couplings and corresponding symmetries in the system. The mass conservation equation (25) constitutes an essential constraint for the stoichiometric coefficients; its neglect may lead to erroneous results. For the transport processes the mass conservation requires that in each elementary process both stoichiometric coefficients are equal

$$\nu_{ki}^{\mathrm{b}} = \nu_{ki}^{\mathrm{f}} \equiv \nu_{ki}^* \tag{27}$$

Nonlinear kinetic equation in the slow diffusion regime

$$r_k = r_k^{\mathrm{f}} - r_k^{\mathrm{b}} = r_k^0\left(\exp\left(-\sum_i \nu_{ki}^* F_i^{\mathrm{f}}\right) - \exp\left(-\sum_i \nu_{ki}^* F_i^{\mathrm{b}}\right)\right) \tag{28}$$

applies the condition (27), which, allegedly as the general one, is sometimes transferred to the realm of chemical reactions. However the equality (27) is inapplicable to genuine chemical reactions; it is valid only to transport processes. Its existence would assure the *identical* vanishing of the chemical affinity, which would imply that the unique equilibrium state cannot be achieved for the chemical equilibrium.

When the process undergoes closely to the equilibrium one can expand the general equation (22) in Taylor series and restrict to the first order deviations of the expansion. This yields

$$r_j \cong r_j^{\mathrm{eq}} \sum_i (\nu_{ji}^{\mathrm{b}} F_i^{\mathrm{b}} - \nu_{ji}^{\mathrm{f}} F_i^{\mathrm{f}}) \tag{29}$$

where the current r_j^{eq} satisfies Eq. (21) at the equilibrium and is the same for both directions.

Thus, in the close vicinity of the equilibrium the reaction rate is proportional to the extended or *nonclassical* affinity A_j. When, additionally, diffusion processes are fast (reactions undergo in the kinetic regime) each reaction rate is proportional to its standard (*classical*) affinity

$$r_j \cong r_j^{\mathrm{eq}} \sum_i (\nu_{ji}^{\mathrm{b}} - \nu_{ji}^{\mathrm{f}}) F_i^* = r_j^{\mathrm{eq}} \sum_i \nu_{ji} F_i^* = r_j^{\mathrm{eq}} A_j^* \tag{30}$$

This shows that closely to equilibrium each reaction rate is uniquely defined by the corresponding affinity of the reaction (which is the *classical* affinity in the kinetic regime). In general, however, a supposition that in any thermodynamic region the reaction rate r_j can uniquely be linked with the chemical affinity A_j by a formula of the type $r = f(A)$ is false. This rate depends on temperature and all concentrations, and, therefore the formuła $r = f(A)$ [similarly as $\mathbf{J} = \mathbf{f}(\mathbf{X})$] is not unique in the general case.

7. Nonlinear coupled transport of mass and heat

Applying models of nonlinear thermokinetics we shall now consider coupled transfer of mass (*m*) and heat (*h*). This process is described by Eq. (28), that contains two expressions. The first one describes the mass flux of an active component (e.g. moisture)

$$r_1 = r_1^0\left(\exp\left[v_{11}^*\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{f}} + v_{12}^*\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{f}}\right] - \exp\left[v_{11}^*\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{b}} + v_{12}^*\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{b}}\right]\right) \quad (31)$$

and the second one—the heat flux $q = r_2$

$$r_2 = r_2^0\left(\exp\left[v_{21}^*\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{f}} + v_{22}^*\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{f}}\right] - \exp\left[v_{21}^*\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{b}} + v_{22}^*\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{b}}\right]\right) \quad (32)$$

Let us determine conditions that must be satisfied in order to assure the Onsager symmetries in the above kinetic equations. Expanding both kinetic expressions in the Taylor series and assuming small driving forces we obtain

$$r_1 = r_1^{\mathrm{eq}}\left(v_{11}^*\left[\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{f}} - \left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{b}}\right] + v_{12}^*\left[\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{f}} - \left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{b}}\right]\right) \quad (33)$$

$$r_2 = r_2^{\mathrm{eq}}\left(v_{21}^*\left[\left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{f}} - \left(\frac{\mu_{\mathrm{m}}}{\mathrm{R}T}\right)^{\mathrm{b}}\right] + v_{22}^*\left[\left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{f}} - \left(-\frac{1}{\mathrm{R}T}\right)^{\mathrm{b}}\right]\right) \quad (34)$$

These equations prove that for a symmetric matrix v_{ki}^* both equilibrium currents r_1^{eq} and r_2^{eq} must be identical, so they must be replaced by a certain universal constant, r^{eq}. If, however, is usual, the discussed matrix is not symmetric then the requirement of Onsagerian symmetries imposes appropriate connections between the currents r_1^{eq} and r_2^{eq}. When memory terms are introduced into the above equations by applying a general approach [23], then these equations can be generalized for processes with finite propagation speeds of signals.

8. Description of reaction rates by a field method applied to a continuum

In considerations describing the motion through the energy barrier the notion of chemical conductance is useful. It is the reciprocal of the standard chemical resistance R_j

$$\Lambda_j(\mathbf{a}, T) \equiv R_j^{-1}(\mathbf{a}, T) = \frac{1}{\mathrm{R}}\frac{r_j^{\mathrm{f}} - r_j^{\mathrm{b}}}{\ln(r_j^{\mathrm{f}}/r_j^{\mathrm{b}})} \quad (35)$$

This formula shows that the chemical conductance is measured by the value of the logarithmic mean of both unidirectional rates. When the one of these rates is close to the other, which takes place in the vicinity of the state of equilibrium, the conductance Λ_j may be approximated by the expression

$$\Lambda_j(\mathbf{a}, T) \cong \frac{1}{2\mathrm{R}}(r_j^{\mathrm{f}} + r_j^{\mathrm{b}}) \cong \frac{r_j^{\mathrm{eq}}}{\mathrm{R}} \quad (36)$$

In terms of Λ_j the chemical Ohm's law that defines the resulting rate of an elementary process has, of course, the form $r_j = \Lambda_j A_j$ where the extended affinity of the entropy representation has the form

$$A_j^{\mathrm{s}} = \sum_{i=1}^{n}(v_{ij}^{\mathrm{b}}F_i^{\mathrm{b}} - v_{ij}^{\mathrm{f}}F_i^{\mathrm{f}}) \quad (37)$$

The relationship $r_j = \Lambda_j A_j$ is an analogue of the Newton–Fourier law, $q = \alpha\Delta T = \alpha(T^{\mathrm{f}} - T^{\mathrm{b}})$, which is well known formula for the heat exchange. The latter is the result of integration of the local Fourier law, $q = -\kappa\,\mathrm{grad}T$, between limits corresponding to a finite difference of temperatures T^{f} and T^{b}. This observation leads to the supposition that the chemical Ohm's law $r_j = \Lambda_j A_j$ may be regarded as a result of the integration of the following vector relationship

$$\mathbf{J}_j = -\lambda_j\mathbf{grad}\Pi_j \equiv \lambda_j\mathbf{grad}\left\{\sum_{i=1}^{n}(Q_{ij}F_i)\right\} \quad (38)$$

along the gradient direction. In the above equation the quantities Π_j defined as

$$\Pi_j \equiv -\sum_{i=1}^{n}(Q_{ij}F_i) \quad (39)$$

are called potentials of the reaction *j*. Let us note that these potentials have the structure of unidirectional components of the chemical affinity. The chemical Ohm's law $r_j = \Lambda_j A_j$ can be recovered from the vector rate formuła (38) by its integration for potentials Π_j between the limits Π_j^{f} and Π_j^{b}. In the rate equation (38), instead of unidirectional stoichiometric coefficients v_{ij}^{f} and v_{ij}^{b} referred to both sides of the energy barrier *stoichiometric variables* Q_{ij} appear (also unidirectional) satisfying the boundary conditions $Q_{ij}^{\mathrm{f}} = v_{ij}^{\mathrm{f}}$ and $Q_{ij}^{\mathrm{b}} = v_{ij}^{\mathrm{b}}$. Let us stress that the introduced approach requires not only the integration with respect to the original potentials F_i, that change in the limits between F_i^{f} and F_i^{b}, but also taking into account changes of stoichiometric functions Q_{ij} between $Q_{ij}^{\mathrm{f}} = v_{ij}^{\mathrm{f}}$ and $Q_{ij}^{\mathrm{b}} = v_{ij}^{\mathrm{b}}$. This approach is reached than the traditional one as it considers properties of the chemical vector (not a scalar) to characterize rates of a definite reaction *j* in the physical space.

For the reaction *j*, we now introduce the molar chemical flux of this reaction, $I_j = \mathrm{d}n_{j\mathrm{prod}}/\mathrm{d}t = V\xi_j/$

dt (d$\xi_j = \mathrm{d}n_{j\mathrm{prod}}/V$), and the density of this flux J_j as the (concentration-based) degree of advancement of the reaction ξ_j referred to the surface A in the unit time. For the reaction at a constant volume the reaction rate r_j satisfies the usual formula $r_j = \mathrm{d}\xi_j/\mathrm{d}t$. In the one-dimensional case one may write $r_j = (AV^{-1})\mathrm{d}n_{j\mathrm{prod}}/A\mathrm{d}t$, whence

$$r_j = I_j/V = (A/V)J_j = (A/V)(J_j^{\mathrm{f}} - J_j^{\mathrm{f}}) \tag{40}$$

where J_j is the resulting (net) density of the chemical flux equal to the difference of the absolute values of the density vector $\mathbf{J}_j$ in states f and b.The relationships between the chemical vector $\mathbf{J}_j$, scalar r_j and (concentration-based) degree of advancement ξ_j are defined by Eqs. (41) and (42) below, in which a remarkable role is played by the production vector of jth reaction, $\mathbf{P}_j$. The chemical vector $\mathbf{J}_j$ is defined by the equations

$$\mathbf{J}_j = \frac{\mathrm{d}\mathbf{P}_j}{\mathrm{d}t} \tag{41}$$

$$\xi_j = \nabla \cdot \mathbf{P}_j \tag{42}$$

The first one explains the name of the vector $\mathbf{P}_j$, whereas the second connects it with the degree of the reaction advancement, $\xi_j = n_{j\mathrm{prod}}/V$. Acting on the first equation with the difference operator and using the second equation one concludes that the scalar rate of the reaction $r_j = \mathrm{d}\xi_j/\mathrm{d}t$ is just the divergence of the vectorial rate

$$\nabla.\mathbf{J}_j = \frac{\mathrm{d}\xi_j}{\mathrm{d}t} = r_j \tag{43}$$

(This result can also be obtained after determining the derivative $\mathrm{d}\xi_j/\mathrm{d}t$ of the second equation and using the first one.) Let us observe, that the integration of both sides of this equation over the volume and making use of the Gauss theorem yields in the one-dimensional case and for a "narrow barrier"

$$r_j = (J_j^{\mathrm{f}} - J_j^{\mathrm{f}})A/V = r_j^{\mathrm{f}} - r_j^{\mathrm{b}} \tag{44}$$

This result is consistent with Eq. (40). It expresses the difference of unidirectional fluxes r^{f} and r^{b} in terms of the change in normal components of the chemical vector $\mathbf{J}_j$, and it proves that for simple boundary conditions, corresponding with one-dimensional motion through the barrier, the previous (thermokinetic) description based on two competing fluxes is recovered. The field description using the chemical vector $\mathbf{J}_j(x,t)$ facilitates to follow the chemical changes, similarly as the field description applying the well known heat flux vector $\mathbf{q}(x,t)$ is useful to observe thermal changes.

Consequently the law of chemical motion can be written in the local form (38) resembling the Fourier law, in which the role of temperature is played by the unidirectional component of the chemical affinity and the reciprocal of specific chemical resistance, Λ_j, plays the role of the heat conductivity. In comparison with the previous approaches considered here, including thermokinetics, we are faced with reorientation, because now the chemical reaction is treated as a transport problem in which the chemical vector $\mathbf{J}_j(\mathbf{x},t)$ is a suitable entity. This approach searches for detailed properties of the motion through the energy barrier by formulating a variational problem of an optimal shape for a "chemical ray" in the physical space, and by solving this problem. In fact, the approach describes a continuous variant of the chemical Fermat principle with an infinite number of infinitesimal refractions of the ray. This is similar to the *continuous* version of the Fermat problem in an optically (or thermally) inhomogeneous medium. The thermally inhomogeneous media have been investigated by this technique in earlier works [24,25].

To expose the kinematic properties of the chemical vector we now present the "law of bending" (Fig. 4) which implies that—by minimizing the total resistance—the chemical ray spanned between two given points takes the shape assuring its relatively large part in a region of lower chemical resistivity (a 'rarer' region of the medium). In effect, the chemical flux bends into the direction that ensures its shape consistent with the longest residence of the chemical complex in regions of lower resistivity. This local principle is here the leading idea to handle highly nonlinear systems. As Eq. (44) holds for a narrow barrier, the local principle recovers previous results in the case of constant specific resistances; on the other hand it is still capable of handling situations in which local properties (including the specific chemical resistance ρ_j) change along the path in a complicated way.

For conserved fluxes the minimum of entropy production is valid that can be associated with the minimum

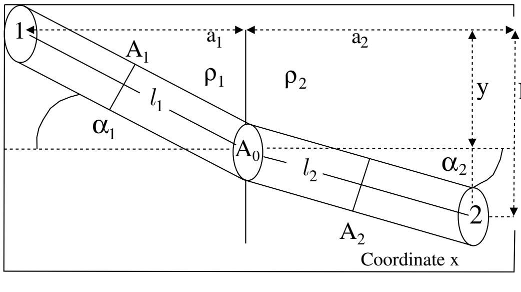

Fig. 4. Illustration of Fermat-type principle of minimum time for a chemical reaction. The chemical motion occurs between two regions with different specific chemical resistances ρ_1 and ρ_2. The path in the coordinates x and y highlights "a chemical ray". The area A_0 tangent to the surface separating two regions of constant ρ (e.g. interface) is a system constant, thus the vertical cross-sections 1 and 2 have a common area A_0. Yet, the areas A_i $(i = 1, 2)$ perpendicular to the chemical flux decrease with angles α_i and are equal $A_0 \cos\alpha_i$.

resistance of the path. Taking this into account it follows that the minimum resistivity at a given flux causes—in the dual picture of the problem—the maximum of flux through the medium along a given path (of a prescribed resistance), which ensures that the residence time of the flux-related charge or reaction complex in the medium is as short as possible. This makes the principle for travel of physical or chemical entities quite similar to that for propagation of light. Our task is to investigate these phenomena by the optimization methods, in particular by variational calculus and dynamic programming.

With the help of the specific chemical resistance ρ_j of a definite reaction, one defines the differential of the total resistance of the path $\mathcal{R}_j$

$$\mathrm{d}\mathcal{R}_j \equiv \rho_j \frac{\mathrm{d}l}{A} \tag{45}$$

The total resistance is the path integral over this expression. Similarly like the electrical resistance the quantity $\mathcal{R}_j$ increases with the total length l and decreases with the cross-sectional area perpendicular to the path A. The chemical Ohm's law for the jth reaction characterized by a *constant* specific resistance ρ_j and flux I_j of the chemical vector $\mathbf{J}_j$ through the area A has the form

$$I_j = \mathcal{R}_j^{-1}(\Pi_j^{\mathrm{f}} - \Pi_j^{\mathrm{b}}) \tag{46}$$

It defines the flux I_j through the surface A as the ratio of the potential difference $\Pi_j^{\mathrm{f}} - \Pi_j^{\mathrm{b}}$ and total resistance $\mathcal{R}_j$. Yet, Eq. (46) is exact only for a constant specific resistance ρ_j which is too special case for the equation to be frequently useful. In fact, the essential role of the variable quantity ρ_j is to replace the physically insufficient (or even artificial) theory based on the *integral* $\mathcal{R}$ of Eq. (46) and rough global Eq. (46) by the *local* formula (38) and a variational principle for a minimum of the total resistance $\mathcal{R}_j$.

In the accepted reference frame the local resistance for the jth chemical flow, ρ_j, changes along the axis x. The axis y is tangent to a surface of constant resistivity $\rho = \text{constant}$. The slope $u = \mathrm{d}y/\mathrm{d}x$ conforms with the local direction of gradient of the Planck potential function, $\Pi_q \equiv \sum_{i=1}^{n} \nu_{iq}\mu_i/T$, that changes in the course of the reaction F $\Longleftrightarrow$ B between $\Pi_q^{\mathrm{f}} = \sum \nu_{iq}^{\mathrm{f}}\mu_i/T$ and $\Pi_q^{\mathrm{b}} = \sum \nu_{iq}^{\mathrm{b}}\mu_i/T$. Clearly, symbols Π^{f} and Π^{b} respectively refer to the substrate and product part of the chemical affinity in the entropy representation. In a special case of single reversible reaction F $\Longleftrightarrow$ B the function in question is the Planck potential itself, $\Pi_q \equiv \mu T^{-1}$, that changes between $\mu_{\mathrm{F}} T^{-1}$ and $\mu_{\mathrm{B}} T^{-1}$. In the chosen reference frame the vector of the gradient of Π_q (or μT^{-1}) lies in the plane x–y, and the surfaces of constant specific resistance are represented by the lines $x = \text{constant}$ (Fig. 4). In these conditions the local direction of the chemical vector $\boldsymbol{I}$ for the reaction F $\leftrightarrow$ B is uniquely determined by the gradient of the Planck function $\Pi_j \equiv \sum \nu_{ij}\mu_i/T$ (Planck potential μT^{-1} in the simplest case of the single reversible reaction).

Chemical Ohm's law associated with the approximate theory based on the *integral* resistance $\mathcal{R}_j$ and approximate (global) equation (46) is now replaced by the *local* formula (consistent with Eq. (38))

$$I_j \equiv V\frac{\mathrm{d}\xi_j}{\mathrm{d}t} = J_j A = -\frac{A\,\mathrm{grad}\Pi_j}{\rho_j} = -\frac{A\mathrm{d}\Pi_j}{\rho_j \mathrm{d}l} = -\frac{\mathrm{d}\Pi_j}{\mathrm{d}\mathcal{R}_j} \tag{47}$$

that admits local variability of the specific resistance ρ_j along the reaction path. Using this formula and the variational principle for minimum total resistance $\mathcal{R}_j$ we shall derive the continuous (field) counterpart of the Fermat law in the form of the bending law for chemical flux, associated with variable ρ_j in formula (47).

In both the discrete and continuous problems $A = A_0 \cos\alpha$ where A_0 is the constant (x-independent) area of the conserved flux tubes intercepted by the interface or any surface of constant ρ_j (Fig. 4), whereas the incidence angle varies with x according to the formula

$$\cos a = \frac{\mathrm{d}x}{\mathrm{d}l} = \frac{\mathrm{d}x}{\sqrt{\mathrm{d}x^2 + \mathrm{d}y^2}} \tag{48}$$

or $\cos\alpha = (\sqrt{(1+u^2)})^{-1}$. In the above equations α is the angle between the gradient of Π (or the chemical ray) and a normal to the planes of constant resistivity. Eqs. (47) and (48) then imply the formulation which describes the vanishing variation for the functional of total resistance defined as

$$\begin{aligned}\mathcal{R}_{1,2} &\equiv \int_{t_1}^{t_2} \rho(x) A_0^{-1} \frac{(\mathrm{d}x^2 + \mathrm{d}y^2)}{\mathrm{d}x^2}\mathrm{d}x \\ &= \int_{x_1}^{x_2} \rho(x) A_0^{-1} (1 + (\mathrm{d}y/\mathrm{d}x)^2)\,\mathrm{d}x\end{aligned} \tag{49}$$

In this functional A_0 is the constant area of projection of the cross-sectional area of the flow tube on the surface of constant resistivity; its constancy is related to the conserved property of the flow. The vanishing variation of resistance is associated with the minimum of the functional (49). Eq. (49) is optimized with respect to the control $u = \mathrm{d}y/\mathrm{d}x$ within each infinitesimal layer $\mathrm{d}x$. Dynamic programming is a general method to set a numerical procedure of optimization [26,27]. The procedure solves the problem of exact determining of chemical wavefronts and chemical rates. The minimum resistance function defined as

$$R_{\mathrm{m}}(x^{\mathrm{i}}, y^{\mathrm{i}}, x^{\mathrm{f}}, y^{\mathrm{f}}) \equiv \min \int_{x^{\mathrm{i}}}^{x^{\mathrm{f}}} A_0^{-1} \rho(x)(1 + u^2)\,\mathrm{d}x \tag{50}$$

satisfies the Hamilton–Jacobi–Bellman equation (HJB equation) of the problem

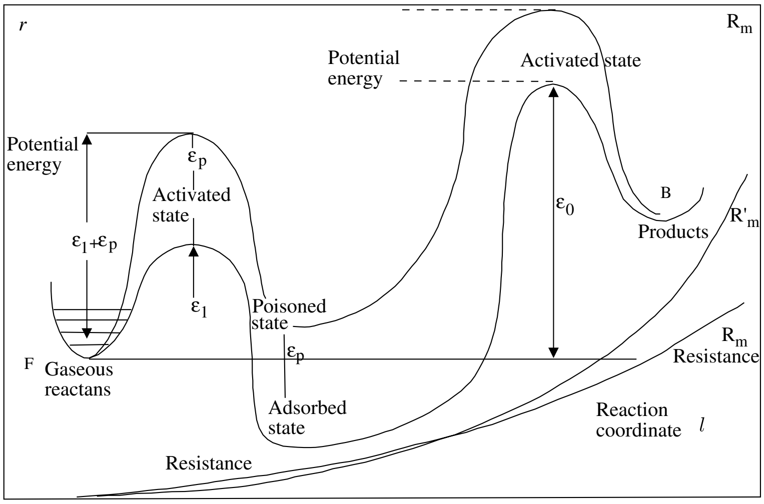

Fig. 5. Potential-energy lines interpreting the role of surface energy of activation and deactivation of catalyst. Increase of optimal cumulative resistance $\mathscr{R}_{\mathrm{m}}$ along the reaction coordinate. The cumulative resistance of the catalytic reaction, optimized in the chemical process, is affected by the state of catalyst.

$$\frac{\partial R_{\mathrm{m}}}{\partial x} + \max_{u}\left\{\frac{\partial R_{\mathrm{m}}}{\partial y}u - A_0^{-1}\rho(x)(1+u^2)\right\} = 0 \tag{51}$$

Extremizing the Hamiltonian bracket in the above equation yields as an optimal control

$$u = \frac{A_0}{2\rho(x)}\frac{\partial R_{\mathrm{m}}}{\partial y} \tag{52}$$

This optimality condition holds for the chemical flow at each point; it is written below in the form of the tangent law of bending for a chemical ray

$$\rho(x)\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{A_0}{2}\frac{\partial R_{\mathrm{m}}}{\partial y} \equiv c, \tag{53}$$

where c is a constant which may be both positive or negative. The constancy of $\partial R/\partial y$ follows from an explicit independence of the chemical Lagrangian with respect to y. Fig. 5 illustrates the cumulative increase of total minimum resistance along the reaction coordinate.

9. Conclusions

The requirement for the chemical (electrochemical) affinity to vanish at equilibrium at every instant of time allows one to define the universal reaction rate constant r_j^0 which constitutes the exchange current of chemical and electrochemical processes. In order to treat electrochemical systems it is sufficient to replace chemical potentials in the Marcelin–de Donder kinetic expressions by electrochemical potentials. The results are nonlinear equations of thermokinetics including, in particular, the Butler–Volmer equation, which is the basic equation of electrochemical kinetics. Applications using the notion of chemical resistances extended to electrochemical systems are remarkable.

General schemes of thermokinetics include to the common model transport effects, in particular, heat transfer. Critical analysis of the literature schemes shows the essential role of constraints following from the mass balance, sometimes ignored in the literature. It also shows the substantial role of nonvanishing differences between unidirectional stoichiometric coefficients for the unique determining of the chemical equilibria.

In spite of the progress represented by the nonlinear termokinetics theory, description of kinetics remains still global, involving finite regions in the physical space and finite driving forces. To describe the chemical transformation as a motion through the energy barrier treated as a continuum an effort was made to replace the logarithmic chemical resistance (a mean quantity associated with a finite affinity or driving force) 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, similar to continuous version of classical Fermat problem in an optically inhomogeneous medium. By considering the case when the chemical resistivity increases with x (the medium becoming "denser" with x) one shows that the slope of the chemical ray decreases with x, thus turning toward the direction of the resistivity gradient. In fact, by minimizing total resistance, the chemical ray spanned between two given points takes the shape that assures that its relatively large part resides in the 'rarer' region of the medium. In other words, the path of chemical complex bends into a direction that ensures its shape associated with longest residence time in regions of lower resistivity. This property makes one possible to predict shapes of chemical rays. This also leads to description of the chemical flows in terms of wavefronts and corresponding Hamilton–Jacobi theory which is derived from a sequential optimization algorithm by the dynamic programming method

Acknowledgement

The authors acknowledge the financial support from the Warsaw TU grant *Dynamics of Complex Systems* in 2003 (stage II of the project).

References

[1] G. Standard, The mass, momentum and energy equations for heterogeneous flow systems, Chem. Eng. Sci. 19 (1964) 227–236.

[2] J. Slattery, Interfacial Transport Phenomena, Springer, Berlin, 1992.

[3] S. Sieniutycz, Nonequilibrium thermodynamics for multiphase reacting systems, in: Proceedings of 3rd Int. Symposium: Catalysis in Multiphase Reactors, 29–31 May 2000, Naples, Italy, AIDIC, 2000, pp. 351–358.

[4] Z. Bilicki, Thermodynamic nonequilibrium in the two-phase system—a continuum with an internal structure, Archiv. Thermodyn. 17 (1/2) (1996) 109–134.

[5] J. Badur, Z. Bilicki, R. Kwidziński, Operacyjna Lepkość Objętościowa w Procesie Transportu Pędu Ekspandującej Wody i Uderzeniowej Kondensacji Pary Wodnej, Zeszyty Naukowe IMP PAN, Gdańsk, 1997.

[6] I. Prigogine, Thermodynamics of Irreversible Processes, Interscience, New York, 1959.

[7] H. Grabert, P. Hänggi, I. Oppenheim, Fluctuations in reversible chemical reactions, Physica 117A (1983) 300–316.

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

[9] S. Sieniutycz, From a least action principle to mass action law and extended affinity, Chem. Eng. Sci. 42 (1987) 2697–2711.

[10] S. Sieniutycz, Variational thermomechanical processes and chemical reactions in distributed systems, Int. J. Heat Mass Transfer 40 (1997) 3467–3485.

[11] L. Onsager, Reciprocal relations in irreversible processes. I, Phys. Rev. 37 (1931) 405–426;
L. Onsager, Reciprocal relations in irreversible processes. II, Phys. Rev. 38 (1931) 2265–2279.

[12] S. Lengyel, I. Gyarmati, Constitutive equations and reciprocity relations of nonideal homogeneous closed chemical systems, Acta Chem. Hung. 122 (1986) 7–17.

[13] J. Keizer, Statistical Thermodynamics of Nonequilibrium Processes, Springer, New York, 1987.

[14] S. Lengyel, Deduction of the Guldberg–Waage mass action law from Gyarmai's governing principle of dissipative processes, J. Chem. Phys. 88 (1988) 1617–1621.

[15] K. Oláh, The way to thermokinetics, ACH—Models Chem. 134 (1997) 343–367.

[16] K. Oláh, Electrode thermokinetics, Period. Polytech. Chem. Eng. 41 (1997) 97–114.

[17] K. Oláh, Reciprocity relations: Maxwell, Onsager. A thermokinetic approach, Period. Polytech. Chem. Eng. 42 (1998) 21–32.

[18] S. Glasstone, K. Leidler, H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.

[19] A. de Vos, Endoreversible Thermodynamics of Solar Energy Conversion, Clarendon Press, Oxford, 1992.

[20] C.M. Guldberg, P. Waage, Etudes Sur Les Affinités Chimiques, Brogger and Christie, Christiana, 1867.

[21] S.R. de Groot, P. Mazur, Nonequilibrium Thermodynamics, Dover, New York, 1984.

[22] J.O'M Bockriss, D.M. Drazic, D.M. Electrochemical Science, Taylor and Francis, London, 1972.

[23] I.M. Shter, The generalized Onsager principle and its application, Inzh. Fiz. Zh. 25 (1973) 736–742.

[24] A. Tan, L.R. Holland, Tangent law of refraction for heat conduction through an interface and underlying variational principle, Am. J. Phys. 58 (1990) 988–991.

[25] S. Sieniutycz, Dynamic programming approach to a Fermat type principle for heat flow, Int. J. Heat Mass Transfer 43 (2000) 3453–3468.

[26] R.E. Bellman, Adaptive Control Processes: a Guided Tour, Princeton University Press, Princeton, 1961.

[27] R. Aris, Discrete Dynamic Programming, Blaisdell, New York, 1964.