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Catalysis Today 79–80 (2003) 307–313

CATALYSIS TODAY

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Extremum properties of interphase chemical reactions in catalytic systems

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Abstract

A variational principle of Fermat type is found for chemical kinetics in inhomogeneous and multiphase reacting systems. The principle is consistent with the notion of ‘intrinsic reaction coordinate’ (IRC), idea of ‘chemical resistance’ (CR) and second law of thermodynamics. The dynamic programming method quantifies the “chemical rays” and related wave-fronts along the reaction coordinate. For the chemical flux, a “law of bending” is found 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.

Keywords: Intrinsic reaction coordinate; Chemical resistance; Catalytic system

1. Introduction

The fundamental assumption of Eyring’s absolute rate theory [1] consist of the existence of the activated complex or transition state C in the course of the chemical reaction F → B so that the chemical mechanism is F ⇔ C → B subject to the chemical equilibrium between F and C. For quantitative studies Fukui [2] have introduced a concept of ‘intrinsic reaction coordinate’ (IRC) as the reaction path from the initial F to final B by way of the transition point C on the adiabatic potential surface, and given the dynamic equations of IRC. In the present work the notion of IRC and the concept of ‘chemical resistance’ (CR) consistent with the mass action law [3] are applied to formulate a Fermat-like principle of minimum time for interphase chemical reactions in nonlinear multiphase systems. (For the definition of the specific CR of an elementary step see our previous (Naples) communication at CAMURE symposium [4] as well as Ref. [3].) To evaluate CRs the contemporary findings in the field of heterogeneous kinetics are exploited [5,6]. The principle is capable of predicting changes in shapes of ‘chemical rays’ (reaction paths) within each phase and through an interface which separates immiscible media. When one phase differs from another in the value of specific CR, ρ, a sort of refraction law describes the bending of ‘chemical rays’ at the interface.

Let us try to describe in a quantitative way a quasi steady-state chemical motion along the reaction path (IRC). The aim is prediction of shapes of chemical paths or “chemical rays” caused by the material inhomogeneity of the medium (media) in which the chemical reaction takes place. Usually macroscopic fluxes are shown to travel along paths satisfying the principle of minimum of entropy production [7,8] which looks quite different than the well-known Fermat principle of minimum time (minimum optical length) for optical rays [9]. However, for conserved fluxes the

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doi:10.1016/S0920-5861(03)00054-3

Nomenclature

$a_i(c_i)$	activity of ith component in terms of its concentration c_i
A	area perpendicular to flow
A_0	constant area of a flux tube intercepted by the interface
$\mathcal{A}^{\mathrm{s}}$	vector of chemical affinities $\mathcal{A}_q^{\mathrm{s}}$ (entropy representation)
I_r	chemical flux or the derivative $\mathrm{d}Q_r/\mathrm{d}t$ for rth reaction
J_q	density of chemical flux of qth reaction, Eq. (2)
l	length coordinate
L_σ	dissipative (thermodynamic) Lagrangian, $\Phi + \Psi$
$\mathcal{L}$	characteristic length for the reaction
N, n	number of reactions and number of species, respectively
Q_j	degree of advancement for jth reaction
r_q	volumetric rate of heterogeneous reaction (qth chain)
R	gas constant
R_j	standard volumetric resistance of jth reaction
$\mathcal{R}$	total chemical resistance of reaction
S, S_σ	entropy and entropy production, respectively
t	time
T	temperature
u	controlled slope $\mathrm{d}y/\mathrm{d}x$, local direction of gradient of Π
V	volume
x, y	horizontal and vertical coordinate, respectively

Greek symbols

α	incidence angle between the gradient of Π and normal to plane of constant ρ
μ_i	molar chemical potential of ith component
ν_{ij}	stoichiometric matrix of jth reaction
Π_{f}, Π_{b}	substrate and product part of chemical affinity
ρ_q	specific chemical resistance of qth heterogeneous reaction
Φ_σ	rate dependent chemical dissipation function
Ψ_σ	state dependent chemical dissipation function

Subscripts

i	ith component
j	step number within a chain
m	minimum
q	number of reacting chain
σ	dissipative property

Superscripts

b	backward
f	forward
s	entropy representation

minimum of entropy production can be associated with the minimum 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, which ensures that the residence time of the flux-related charge 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 of variational calculus [10,11] and dynamic programming [12,13].

2. Thermodynamics and CR of a heterogeneous reaction system

We apply here the same description as in our previous publication [4]. Each phase is an open, multi-component system, of n components and N chemical reactions:

$$\sum_{i=1}^{n}\nu_{ij}^{\mathrm{f}}[i] \leftrightarrow \sum_{i=1}^{n}\nu_{ij}^{\mathrm{b}}[i], \quad i = 1, \dots, n, \ \ j = 1, \dots, N$$

The system contains species i with chemical potential μ_i, and T is the local temperature. The ν_{ij}^{f} and ν_{ij}^{b} are the forward and backward stoichiometric coefficients, respectively, for species i in reaction j. The advancement of the jth elementary reaction is denoted by Q_j, and its volumetric rate r_j. Similarly the advancement of the qth heterogeneous reaction (a chain of elementary steps) is denoted by Q_q, and its rate r_q.

In the development of nonequilibrium thermodynamics of chemical systems a mathematical condition is known for an entropy-like state function to be generated along kinetic paths; the rate dependent dissipation function Φ_σ has to be numerically equal to the state dependent dissipation function Ψ_σ. In the physical space–time, the following structure of the entropy production is valid for all real kinetic paths (satisfying $\Phi_\sigma = \Psi_\sigma$):

$$S_\sigma = \int_{t_1,V}^{t_2} L_\sigma \, \mathrm{d}V \, \mathrm{d}t = \int_{t_1,V}^{t_2} (\Phi_\sigma + \Psi_\sigma) \, \mathrm{d}V \, \mathrm{d}t$$
$$= \int_{t_1,V}^{t_2} 2\Phi_\sigma \, \mathrm{d}V \, \mathrm{d}t = \int_{t_1,V}^{t_2} \Sigma r_q^2 R_q \, \mathrm{d}V \, \mathrm{d}t \qquad (1)$$

where the summation is over the reaction index q and R_q is the standard (volumetric) CR of the complex reaction q in the entropy representation [11]. (In our previous publications [4] the standard resistance was referred to jth elementary reaction and designated by the symbol R_j.) Here we are also using a related specific quantity ρ_q, defined in Eq. (2), and the total resistance $\mathcal{R}_q$, defined in Eq. (4)). We stress the need to clearly distinguish between these resistances.

The activated complex is transferred along the length dl of the reaction path by a cross-section of the area A that is perpendicular to the chemical flux. As shown in Fig. 1, perpendicular cross-sections in phases 1 and 2 may be different; they have the areas A_1 or A_2. In a corresponding continuous problem A may change continuously with l; the related volume differential $\mathrm{d}V = A\,\mathrm{d}l$. For the reaction q, we introduce the chemical current of this reaction, $I_q = \mathrm{d}Q_q/\mathrm{d}t$, as its degree of advancement referred to the area A per unit time. (In the present formalism the advancement variables play role of charges hence the notation.) The density of the chemical flux q satisfies the usual formula $r_q = \mathrm{d}Q_q/V\,\mathrm{d}t$. One can also write $r_q = (A/V)\,\mathrm{d}Q_q/A\,\mathrm{d}t$ or $r_q = I_q/V = (A/V)J_q$, where J_q is the chemical flux. Two alternative forms of the entropy production are then obtained

$$S_\sigma = \int_{t_1,V}^{t_2} \Sigma R_q r_q^2 \, \mathrm{d}V \, \mathrm{d}t = \int_{t_1,V}^{t_2} \Sigma R_q \left(\frac{A}{V}\right)^2 J_q^2 \, \mathrm{d}V \, \mathrm{d}t$$
$$= \int_{t_1,V}^{t_2} \Sigma \rho_q J_q^2 \, \mathrm{d}V \, \mathrm{d}t \qquad (2)$$

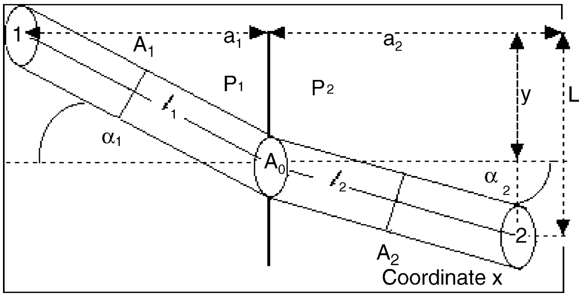

Fig. 1. Illustration of Fermat-type principle of minimum time for a catalytic chemical reaction. The chemical motion occurs between two regions with different specific CRs ρ_1 and ρ_2. The path in the coordinates x and y highlights "a chemical ray". The area A_0 tangent to the surface separating two 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 $A_0 \cos\alpha_i$.

In an inhomogeneous case one may use the variable ρ_q to treat the process locally, as a function of a suitable length coordinate l (IRC) or x. Consequently

$$S_q = \int_{t_1,V}^{t_2} \rho \left(\frac{\mathrm{d}Q}{A\,\mathrm{d}t}\right)^2 \mathrm{d}V \, \mathrm{d}t$$
$$= \int_{t_1,V}^{t_2} (\rho \, \mathrm{d}l) \left(\frac{\mathrm{d}Q}{A\,\mathrm{d}t}\right)^2 A \, \mathrm{d}t$$
$$= \int_{t_1,l}^{t_2} \left(\frac{\rho}{A}\mathrm{d}l\right) \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^2 \mathrm{d}t \qquad (3)$$

where, for simplicity, we have neglected the reaction index q at the specific CR ρ. This simplification is also made below in several other formulas of this sort. The total entropy production S_σ is the sum of the above expressions for all chemical reactions, i.e. $S_\sigma = \sum S_q$, with the summation with respect to the reaction index q.

As ρ has the meaning of the specific CR, the differential expression

$$\mathrm{d}\mathcal{R} \equiv \rho \frac{\mathrm{d}l}{A} \qquad (4)$$

defines the first differential of the total CR $\mathcal{R}$. The situation is analogous to that in an electric circuit system. The total resistance itself is the path integral of (4). Similarly as electric resistance, the quantity $\mathcal{R}$ increases with total length l and decreases with cross-sectional area A. With the definition (4) Eq. (3)

can be transformed into a familiar (Joule–Onsager) form that describes the generation of entropy within the system. In terms of $\mathcal{R}$ the entropy production of qth reaction is

$$S_q = \int_{t_1,V}^{t_2} \left(\frac{\rho}{A}\right) \mathrm{d}l \int_{t_1}^{t_2} \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)^2 \mathrm{d}t = \int_{Q_1}^{Q_2} \mathcal{R} I \, \mathrm{d}Q = \int_{Q_1}^{Q_2} (\Pi^{\mathrm{f}} - \Pi^{\mathrm{b}}) \, \mathrm{d}Q = \int_{t_1}^{t_2} \mathcal{R} I^2 \, \mathrm{d}t \tag{5}$$

A heterogeneous reaction is viewed as the transformation of substrates from phase f (lauching forward reactions) into products in phase b (lauching backward reactions). A simple example can be an electrochemical reaction in which a positively charged ion of a metal is transferred form the crystal grid (phase f) into the electrolyte solution (phase b). In formula (5), symbols Π^{f} and Π^{b}, respectively, refer (in the entropy representation), to the substrate and product part of the chemical affinity evaluated for an overall or resulting reaction q; consider the two additive terms in Eq. (6). These parts are obtained as if the resulting reaction was homogeneous; see the previous results [3,4]. The resulting chemical affinity of a chain reaction system and the specific CR of this resulting chain reaction depend on concentrations c_i (affinities a_i). In a consecutive chain of several elementary steps (qth chemical chain), the overall chemical affinity of the chain is

$$\mathcal{A}_q^{\mathrm{s}} = \sum_{i=1}^{n} \frac{(\nu_{iq}^{\mathrm{f}} - \nu_{iq}^{\mathrm{b}})\mu_i}{T} = -\sum_{i=1}^{n} \frac{\nu_{iq}\mu_i}{T} = R \ln\left[k_q^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{f}}}\right] - \ln\left[k_q^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{b}}}\right] \tag{6}$$

in the entropy representation. Whereas the specific resistance formula for this overall (non-elementary) reaction in the form corresponding with the Langmuir–Hinshelwood mechanism of kinetics [5,6] with its heterogeneous inhibiting term is

$$\rho_q(\mathbf{a}, T) = R\mathcal{L}^{-2} \frac{\ln\left(k_q^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{f}}}\right) - \ln\left(k_q^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{b}}}\right)}{k_q^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{f}}} - k_q^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{b}}}} \times \left(1 + k_q^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{f}}} + k_q^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{iq}^{\mathrm{b}}}\right)^{\Sigma \nu_{iq}^{\mathrm{f}}} \tag{7}$$

From Eq. (6) the substrate and product part of the chemical affinity, i.e. terms Π^{f} and Π^{b} in Eq. (5), follow as forward and backward contributions in formula (6). Eq. (8) is, in fact, the consistency condition for the resulting kinetics with the Langmuir–Hinshelwood kinetics and also (when taking into account individual separate steps) with the mass action law [3]. Consistently with Eqs. (7) and (8), the entropy-representation Ohm's law of the qth reaction chain characterized by the constant resistance $\mathcal{R}_q$ and chemical flux I_q is

$$I_q = \mathcal{R}_q^{-1}(\Pi_q^{\mathrm{f}} - \Pi_q^{\mathrm{b}}) \tag{8}$$

which expresses the current through the area A as ratio of the potential difference $\Pi_q^{\mathrm{f}} - \Pi_q^{\mathrm{b}}$ to the total resistance, $\mathcal{R}_q$. Eq. (8) only holds for a constant ρ. This case is, however, too special to be important. In fact, the essential role of the (variable) quantity ρ is to replace the physically insufficient (or even artificial) theory based on the integral $\mathcal{R}$ of Eq. (4) and rough global Eq. (8) by the local formula (4) and a variational principle.

3. A discrete problem of minimum resistance

In Fig. 1 the reaction flow is the travel between two fixed points, 1 and 2. If A_0 is the constant area of a flux tube intercepted by the interface (the constant area of projection of the flux tube cross-sectional area on the surface of constant resistance), then the cross-sectional areas of the flux tubes in the two media are $A_i = A_0 \cos\alpha_i$. The total resistance follows from the system geometry as

$$R_{1,2} = \frac{1}{A_0}\left(\frac{\rho_1(a_1^2 + y^2)}{a_1} + \frac{\rho_2(a_2^2 + (L-y)^2}{a_2}\right) \tag{9}$$

Since in Fig. 1 $y/a_1 = \tan\alpha_1$ and $(L-y)/a_2 = \tan\alpha_2$, the condition requiring the first derivative $\mathrm{d}R_{1,2}/\mathrm{d}y$ to vanish has the form

$$\frac{\mathrm{d}R_{1,2}}{\mathrm{d}y} = \frac{2}{A_0}\left(\frac{\rho_1 y}{a_1} - \frac{\rho_2(L-y)}{a_2}\right) = 0 \tag{10}$$

This is equivalent with the requirement that the tangent law of bending

$$\rho_1 \tan\alpha_1 = \rho_2 \tan\alpha_2 \tag{11}$$

is satisfied for the chemical flux I. The second derivative of $R_{1,2}$ is positive, thus the extremum point is a minimum. This is analogous to Snell's law or refraction in optics but with the tangent replacing the sine and the resistivity replacing the refractive index.

4. A continuous problem of minimum resistance

For a quasi-steady process in the entropy generation (3) can be given the form

$$P_\sigma = \frac{S_\sigma}{t_2 - t_1} = \int_{t_1}^{t_2} (\rho I^2 A^{-1})\,\mathrm{d}l = \int_{t_1}^{t_2} p\,\mathrm{d}l \qquad (12)$$

where $p = \rho I^2 A^{-1}$ and $u = \mathrm{d}y/\mathrm{d}x$ is the slope of the tangent to the path. In the accepted reference frame the local resistance for the chemical flow, ρ, 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 ⇔ B between $\Pi_q^{\mathrm{f}} \equiv \sum \nu_{iq}^{\mathrm{f}}\mu_i/T$ and $\Pi_q^{\mathrm{b}} \equiv \sum \nu_{iq}^{\mathrm{b}}\mu_i/T$. In a special case of single reversible reaction F ⇔ 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. 1).

Extremum conditions that hold locally within each phase are also applied to interfaces. Following the results obtained above and our earlier work for the conserved energy transfer [13] one can derive a ‘law of refraction’ for a chemical flux from boundary conditions that apply the continuity of the Planck potential function and the mass conservation across the interface. Under these conditions and for the reaction F → B the local direction of the chemical flow I is uniquely determined by the gradient of the Planck function, $\Pi_q \equiv \sum \nu_{iq}\mu_i/T$ (Planck potential μT^{-1} in the simplest case of a single reversible reaction). The “discrete” law of bending for conduction of conserved chemical rays follows as ratio of these conditions in the form (11). However, in this section we are interested in continuous counterpart of this law associated with the chemical transfer formula

$$I^j \equiv \frac{\mathrm{d}Q^j}{\mathrm{d}t} = J^j A = -\frac{A\,\mathrm{grad}\,\Pi_j}{\rho_j} = -\frac{A\,\mathrm{d}\Pi_j}{\rho_j\,\mathrm{d}l} = -\frac{\mathrm{d}\Pi_j}{\mathrm{d}\mathcal{R}_j}. \qquad (13)$$

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 surfact of constant ρ (Fig. 1), whereas the incidence angle varies with x according to the formula

$$\cos\alpha = \frac{\mathrm{d}x}{\mathrm{d}l} = \frac{\mathrm{d}x}{\sqrt{\mathrm{d}x^2 + \mathrm{d}y^2}} \qquad (14)$$

or $\cos\alpha = (1+u^2)^{-1/2}$. 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. (13) and (14) then imply the formulation which describes the vanishing variation for the functional of total resistance defined as

$$\mathcal{R}_{1,2} = \int_{t_1}^{t_2} \left(\frac{\rho(x)(\mathrm{d}x^2 + \mathrm{d}y^2)}{A_0\,\mathrm{d}x^2}\right)\mathrm{d}x = \int_{x_1}^{x_2} A_0^{-1}\rho(x)\left(1 + \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2\right)\mathrm{d}x \qquad (15)$$

Dynamic programming method is applied [12,13] to set a general numerical procedure that solves the problem of exact calculation of chemical fronts and chemical rates. The shape of conserved chemical rays is described as an optimal control problem for a minimum of the entropy production (12) in case of the conserved chemical flux I in which case the function $p(x, y, u) = A_0\rho(x)\sqrt{1+u^2}$ (Eqs. (12) and (15)). In this function 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 a transferred flux. For the considered function p the vanishing variation in Eq. (19) is associated with the minimum of the functional (15). Eq. (15) should be optimized with respect to the control $u = \mathrm{d}y/\mathrm{d}x$ within each infinitesimal layer dx. The reader is referred to literature for the detailed analytical [10] and numerical [13] studies of Eq. (15). The minimum resistance function defined as

$$R_{\mathrm{m}}(x^i, y^i, x^f, y^f) = \min \int_{x^i}^{x^f} A_0^{-1}\rho(x)(1+u^2)\,\mathrm{d}x \qquad (16)$$

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

$$\frac{\partial R_{\mathrm{m}}}{\partial x} + \max_u \left\{\frac{\partial R_{\mathrm{m}}}{\partial y}u - A_0^{-1}\rho(x)(1+u^2)\right\} = 0 \qquad (17)$$

The model composed of Eqs. (16) and (17), follows from the continuous dynamic programming algorithm

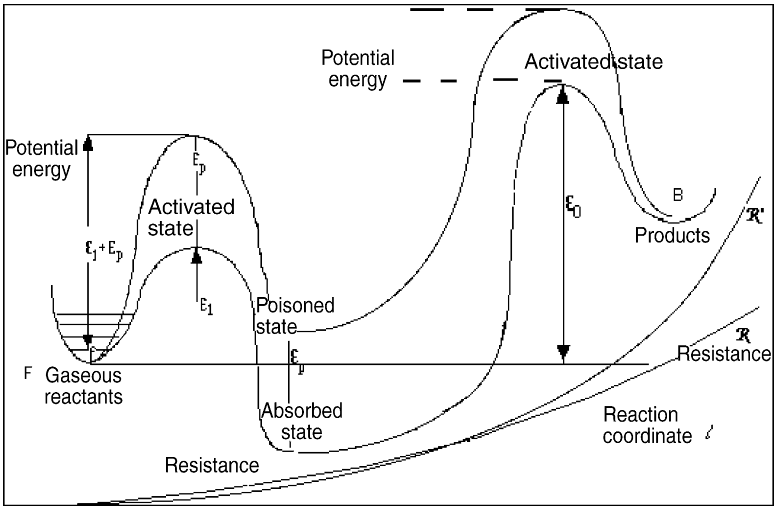

Fig. 2. Potential energy lines interpreting the role of surface energy of activation and deactivation of catalyst. Increase of optimal cumulative resistance R_m along the reaction coordinate. The cumulative resistance of the catalytic reaction, optimized in the chemical process, is affected by the state of catalyst.

applied to the performance criterion (15). Extremizing the Hamiltonian bracket in the above equation yields as an optimal control

$$u = \frac{A_0}{2\rho(x)} \frac{\partial R_m}{\partial y} \tag{18}$$

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 conserved chemical ray

$$\rho(x)\frac{dy}{dx} = \frac{A_0}{2}\frac{\partial R_m}{\partial y} \equiv c \tag{19}$$

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. 2 illustrates the cumulative increase of total resistance along the reaction coordinate. To show how the method works in some detail, we refer the reader to our previous work [4] that describes the process of creation of the new phase (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. Second-law variational principle which uses the suitable resistance applies therein to pseudo-homogeneous mixture of water and vapor. This leads to the description of flashing as an interface chemical reaction.

5. Concluding remarks

In agreement with basic principles of thermodynamics and Onsager's theory we showed here existence of a Fermat-like principle for heterogeneous chemical systems. The tangent law of bending that holds for conserved chemical flows (chemical complex) is different from Snell's law of refraction in optics, with the tangents of the angles of incidence and refraction replacing the sines and the reciprocal of the Onsager's conductivity taking the place of the refractive index. 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 wave-fronts and corresponding Hamilton–Jacobi theory which is derived from a sequential optimization algorithm of the dynamic programming method.

Acknowledgements

This work was supported by a dean's grant in 2002.

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