

Multiple Rate-Determining Steps for Nonideal and Fractal Kinetics<sup>†</sup>Marcel O. Vlad,<sup>\*,‡,§</sup> Vlad T. Popa,<sup>||</sup> E. Segal,<sup>⊥</sup> and John Ross<sup>‡</sup>

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We show that the kinetic model of a single rate-determining step in a reaction mechanism can be extended to systems with multiple overall reactions for which the elementary reactions obey nonideal or fractal kinetics. The following assumptions are necessary: (1) The system studied is either closed or open, but no constraints exist preventing the evolution toward equilibrium. (2) Elementary reactions occur in pairs of forward and backward steps. (3) The kinetics of the elementary steps are either nonideal or fractal and are compatible with equilibrium thermodynamics. (4) The number of reaction routes is identical with the number of rate-determining steps. If these hypotheses are valid, then the overall reaction rates can be explicitly evaluated: they have a form similar to the kinetic equations for the elementary reactions and the apparent reaction orders and fractal coefficients can be expressed analytically in terms of the kinetic parameters of the elementary reactions. We derive a set of relationships which connect the equilibrium constants of the reaction routes, the corresponding overall rate coefficients, and the stoichiometric numbers of the rate-determining steps. We also derive a set of generalized Boreskov relations among the apparent activation energies of the forward and backward overall processes, the corresponding reaction enthalpies, and the stoichiometric coefficients of the rate-determining steps. If the elementary reactions obey fractal kinetics, the same is true for the rate-determining steps. The fractal exponents of the forward and backward overall reactions are linear combinations of the fractal exponents of the fractal elementary reactions. Similar to the theory of single rate-determining steps, our approach can be used for selecting suitable reaction mechanisms from experimental data.

## 1. Introduction

The theory of reaction routes is an important theoretical tool for understanding the kinetics of complicated reaction systems.<sup>1–6</sup> This theory provides a rational basis for the description of complicated reaction networks in terms of overall reactions. The theory of the rate-determining step is an important particular case of the reaction routes theory; a rate-determining step, if there is one, leads to simplified kinetic equations and to simple rules for selecting appropriate reaction mechanisms compatible with experimental data. The rate-determining-step approximation has been applied to various reaction systems, many of them of practical, industrial importance.<sup>3–6</sup>

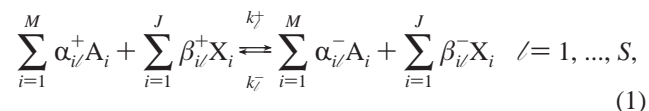
In this paper, we investigate the possibilities of generalizing the rate-determining-step approach to systems with multiple reaction routes for which the elementary steps obey nonideal or fractal kinetics. Three of us studied a particular case of this problem almost fifteen years ago;<sup>7</sup> we limited ourselves to the particular case where the elementary reaction obey ideal mass action law. The theory presented in ref 7 was entirely kinetic and based on multidimensional multiplicative linear algebra. Fortunately by using suitable definitions of the kinetic parameters, the kinetic equations for nonideal and fractal systems can

be made isomorphic with the equations used in ref 7 and thus we can easily adapt these equations for the more general cases of nonideal and fractal kinetics and multiple rate-determining steps equal to the number of possible reaction rates.

The structure of the paper is the following. In section 2, we summarize the main results derived in ref 7 for ideal kinetics. Sections 3 and 4 deal with nonideal and fractal kinetics, respectively.

## 2. Multiple Rate-Determining Steps for Ideal Systems

In ref 7, we considered a complex chemical process involving  $S$  elementary steps



with

$$3 \geq \sum_{i=1}^M \alpha_{i\ell}^{\pm} + \sum_{i=1}^J \beta_{i\ell}^{\pm} \geq 1 \quad \ell = 1, \dots, S, \quad (2)$$

where  $A_i$  are stable species,  $X_i$  are active intermediates,  $\alpha_{i\ell}^{\pm} \geq 0$ ,  $\beta_{i\ell}^{\pm} \geq 0$  are stoichiometric coefficients, and  $k_{\ell}^{\pm}$  are forward and backward rate coefficients, respectively.

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The elementary reactions (eq 1) need not be linearly independent but only physically independent; the stoichiometric vectors

$$\mathbf{f}_{M+J}^{(\ell)} = \begin{pmatrix} \mathbf{a}_M^{(\ell)} \\ \mathbf{b}_J^{(\ell)} \end{pmatrix} \quad \ell = 1, \dots, S, \quad (3)$$

with

$$\mathbf{a}_M^{(\ell)} = (a_{i\ell})_{i=1,\dots,M} \quad a_{i\ell} = \alpha_{i\ell}^- - \alpha_{i\ell}^+ \quad \ell = 1, \dots, S, \quad (4)$$

$$\mathbf{b}_J^{(\ell)} = (b_{i\ell})_{i=1,\dots,J} \quad b_{i\ell} = \beta_{i\ell}^- - \beta_{i\ell}^+ \quad \ell = 1, \dots, S, \quad (5)$$

may be linearly dependent. It follows that the rank  $\mathcal{H}$  of the stoichiometric matrix

$$\mathbf{F}_{M+J,S} = (\mathbf{f}_{M+J}^{(1)}, \dots, \mathbf{f}_{M+J}^{(S)}) = (f_{ij})_{i=1,\dots,M+J}^{j=1,\dots,S} = \begin{pmatrix} \mathbf{a}_{M,S} \\ \mathbf{b}_{J,S} \end{pmatrix} \quad (6)$$

obeys the inequality

$$\text{rank} \mathbf{F}_{M+J,S} = \mathcal{H} \leq \min(M + S, J) \quad (7)$$

where  $\mathbf{a}_{M,S}$  and  $\mathbf{b}_{J,S}$  are partitions of the stoichiometric matrix  $\mathbf{F}_{M+J,S}$  corresponding to stable species and active intermediates, respectively.

According to Horiuti,<sup>1-2</sup> starting from the elementary reactions (eq 1), we can obtain overall reactions (reaction routes) by multiplying each of eq 1 by a stoichiometric number  $\sigma_\ell$  summing over  $\ell$  and requiring that in the resulting overall reaction the coefficients of the active intermediates  $X_i$  be zero. This condition leads to an undetermined homogeneous system of linear equations in the stoichiometric numbers  $\sigma_\ell$ . The number  $P$  of independent solutions of this homogeneous system is the number of reaction routes (overall reactions) necessary for the kinetic description of the system in terms of the stable species  $A_i$ . According to the Horiuti–Nakamura theorem,<sup>2</sup> which is a kinetic analogue of Gibbs phase rule, the number  $P$  of reaction routes is given by  $P = S - I$ , where  $I$  is the number of independent intermediates (in the Horiuti sense), that is

$$I = \text{rank} \mathbf{B}_{J,S}, \quad (8)$$

with

$$\mathbf{B}_{J,S} = (\mathbf{b}_J^{(1)}, \dots, \mathbf{b}_J^{(S)}) = (b_{i\ell})_{i=1,\dots,J}^{\ell=1,\dots,S} \quad (9)$$

being a partition of the stoichiometric matrix which corresponds to the active intermediates.

In ref 7, we have shown that the theory of the rate-determining step can be extended to multiple overall reactions provided that the following conditions are fulfilled:

- (1) The system studied is either closed or open, but no constraints preventing the evolution toward equilibrium exist.
- (2) Elementary steps occur in pairs of forward and backward reactions.
- (3) The kinetics of elementary reactions obeys the classical form of the mass-action law.
- (4) The number of reaction routes  $P$  is identical with the number of rate-determining steps.

Under these circumstances, the net reaction rates of the elementary steps (eq 1) are given by

$$r_\ell = r_\ell^+ - r_\ell^- \quad \ell = 1, \dots, S \quad (10)$$

with

$$r_\ell^\pm = k_\ell^\pm \prod_{i=1}^M [A_i]^{\alpha_{i\ell}^\pm} \prod_{i=1}^J [X_i]^{\beta_{i\ell}^\pm} \quad \ell = 1, \dots, S, \quad (11)$$

Denoting by  $\sigma_{u,\ell}$  the stoichiometric number of the elementary reaction  $\ell$  from the overall reaction  $u$ , we can express the overall reaction rates  $\tilde{r}_u$  as

$$\tilde{r}_u = \sum_{\ell=1}^S \sigma_{u,\ell} r_\ell \quad u = 1, \dots, P \quad (12)$$

Out of the  $S$  elementary steps (eq 1),  $P$  are rate-determining steps and  $S - P$  are in quasi-equilibrium. Without loss of generality, we can order the reactions (eq 1) so that the first  $S - P$ ,  $\ell = 1, \dots, S - P$  are in quasi-equilibrium and the remaining  $P$ ,  $\ell = S - P + 1, \dots, S$  are rate determining. It follows that

$$r_\ell^+ \cong r_\ell^- \quad \ell = 1, \dots, S - P \quad (13)$$

The choice of a set of overall reactions is not unique.<sup>1-6</sup> Without loss of generality, we can choose a set of overall reactions so that each of the  $P$ -determining steps  $\ell = S - P + 1, \dots, S$  occurs on only one of the  $P$  reaction routes. Under these circumstances, from eqs 12–13, the  $P$  overall reaction rates can be expressed as

$$\tilde{r}_u = \tilde{r}_u^+ - \tilde{r}_u^- \quad (14)$$

with

$$\tilde{r}_u^\pm = \frac{r_{S-P+u}^\pm}{\sigma_{S-P+u,u}} = (\sigma_{S-P+u,u})^{-1} k_{S-P+u}^\pm \prod_{i=1}^M [A_i]^{\alpha_{i,S-P+u}^\pm} \prod_{i=1}^J [X_i]^{\beta_{i,S-P+u}^\pm} \quad (15)$$

Similarly, the quasi-equilibrium conditions (eq 13) lead to

$$k_\ell^+/k_\ell^- = \prod_{i=1}^M [A_i]^{\alpha_{i\ell}} \prod_{i=1}^J [X_i]^{\beta_{i\ell}} \quad \ell = 1, \dots, S - P \quad (16)$$

The evaluation of the overall reaction rates  $\tilde{r}_u$  reduces to the elimination of the concentrations  $[X_i]$ ,  $i = 1, \dots, J$  of the active intermediates from eqs 15–16. Since  $J \geq I = \text{rank} \mathbf{B}_{J,S} = S - P$ , there are two different cases: (a)  $J = S - P$  and (b)  $J > S - P$ . For  $J = S - P$ , we take logarithms in eq 16, resulting in an inhomogeneous system of linear equations in  $\ln[X_i]$  with a nonsingular square matrix which can be solved exactly. For  $J > S - P$ , the concentrations  $[X_i]$  cannot be evaluated from eq 18. However, both eqs 15 and 16 can be expressed in terms of a set of multiplicative Horn complexions<sup>8</sup> of the type  $\prod_{i=1}^J [X_i]^{b_{ij}}$  and these complexions can be evaluated from eq 16, making it possible to compute the overall reaction rates. In both cases, the expressions for the rates of the overall reactions are

$$\tilde{r}_u^\pm = \tilde{k}_u^\pm \prod_{i=1}^M [A_i]^{n_{iu}^\pm}, \quad (17)$$

where

$$\tilde{k}_u^\pm = \frac{k_{S+P-u}^\pm}{\sigma_{S+P-u,u}} \prod_{\ell=1}^{S-P} \left( \frac{k_\ell^+}{k_\ell^-} \right)^{\sum_{i=1}^{S-P} (\mathbf{B}_{S-P,S-P})_{\ell}^{-1} \beta_{S-P+u}^\pm} \quad (18)$$

are overall forward and backward rate coefficients, respectively

$$\mathbf{n}_{M,P}^\pm = (n_{iu}^\pm) = \alpha_{M,P}^\pm - \mathbf{a}_{M,S-P} \mathbf{B}_{S-P,S-P}^{-1} \beta_{S-P,P}^\pm, \quad (19)$$

are the vectors of the overall reaction orders,  $\alpha_{M,P}^\pm$  and  $\beta_{S-P,P}^\pm$  are matrices of stoichiometric coefficients defined by

$$\alpha_{M,P}^\pm = (\alpha_{i\ell}^\pm)_{i=1,\dots,M}^{\ell=1,\dots,P} \quad \beta_{S-P,P}^\pm = (\beta_{i\ell}^\pm)_{i=1,\dots,S-P}^{\ell=1,\dots,P} \quad (20)$$

$\mathbf{a}_{M,S-P}$  is a submatrix of the submatrix  $\mathbf{a}_{M,S}$  of the stoichiometric matrix  $\mathbf{F}_{M+J,S}$

$$\mathbf{a}_{M,S} = (\mathbf{a}_{M,S-P}; \mathbf{a}_{M,P}) \quad (21)$$

and  $\mathbf{B}_{S-P,S-P}$  is a square nonsingular partition of  $\mathbf{B}_{J,S}$

$$\mathbf{B}_{J,S} = \begin{pmatrix} \mathbf{B}_{S-P,S-P} & \mathbf{B}_{S-P,P} \\ \mathbf{B}_{J-S+P,P} & \mathbf{B}_{J-S+P,P} \end{pmatrix} \quad (22)$$

with rank  $\mathbf{B}_{S-P,S-P} = S - P$ .

The equilibrium conditions for the overall reactions

$$\tilde{r}_u = 0 \quad u = 1, \dots, P, \quad (23)$$

leads to a set of relationships between the overall rate coefficients  $\tilde{k}_u^\pm$  and the equilibrium constants  $\tilde{K}_u^{\text{eq}}$  of the overall reactions

$$\tilde{k}_u^+ / \tilde{k}_u^- = (\tilde{K}_u^{\text{eq}})^{1/\sigma_{S-P+u,u}} \quad (24)$$

Equation 24 is a generalization of the Horiuti relation for a single rate-determining step.<sup>1</sup>

In conclusion, in this section, we presented a summary of our previous research on multiple rate-determining steps for ideal kinetics. These results are used in the following section for extending the theory of rate-determining step to nonideal and fractal kinetics.

### 3. Multiple Rate-Determining Steps for Nonideal Systems

The study of reaction kinetics in concentrated systems is an old topic of chemical kinetics. Initially, research on this direction was related to the study of salt effects in ionic solutions.<sup>9</sup> Further theoretical developments were based on transition-state theory.<sup>10</sup> A naïve approach would suggest that kinetic laws of eq 11 can be applied to concentrated systems provided that the chemical concentrations  $[A_i]$  and  $[X_i]$  are replaced by the corresponding thermodynamic activities  $\mathcal{A}_i$  and  $\mathcal{X}_i$ . However, experimental and theoretical studies have shown that this is not the case.<sup>9–10</sup> Suitable expressions for the reaction rates in concentrated systems have the form

$$r_\ell^\pm = k_\ell^\pm \varphi_\ell^\pm((\mathcal{A}_i), (\mathcal{X}_i)) \prod_{i=1}^M (\mathcal{A}_i)^{\alpha_{i\ell}^\pm} \prod_{i=1}^J (\mathcal{X}_i)^{\beta_{i\ell}^\pm} \quad \ell = 1, \dots, S \quad (25)$$

where the  $k_\ell^\pm$  values are rate coefficients for infinite dilution

and  $\varphi_\ell^\pm((\mathcal{A}_i), (\mathcal{X}_i))$  are activity correction factors which tend toward one for very dilute systems

$$\varphi_\ell^\pm((\mathcal{A}_i), (\mathcal{X}_i)) \rightarrow 1 \quad \text{as} \quad \forall \mathcal{A}_i, \mathcal{X}_i \rightarrow 0. \quad (26)$$

The most popular interpretation of eq 25 is based on the use of the transition-state theory;<sup>10</sup> in this case, the factors  $\varphi_\ell^\pm((\mathcal{A}_i), (\mathcal{X}_i))$  are inversely proportional to the activity coefficient of the transition state. In order for the kinetic eqs 25–26 to be compatible with equilibrium thermodynamics, we must have

$$\varphi_\ell^+((\mathcal{A}_i), (\mathcal{X}_i)) = \varphi_\ell^-((\mathcal{A}_i), (\mathcal{X}_i)) = \varphi_\ell((\mathcal{A}_i), (\mathcal{X}_i)). \quad (27)$$

Concerning the generalization of the rate-determining step for systems with multiple overall reactions, all assumptions presented in section 2 remain valid, excepting that the elementary kinetic laws (eq 11) are replaced by eqs 25–26. We notice that the concentrations of active intermediates are usually low, and thus it is reasonable to assume that the functions  $\varphi_\ell((\mathcal{A}_i), (\mathcal{X}_i))$  are independent of  $\mathcal{X}_i$

$$\varphi_\ell((\mathcal{A}_i), (\mathcal{X}_i)) = \varphi_\ell((\mathcal{A}_i)) \quad \text{independent of } \mathcal{X}_i \quad (28)$$

Our approach can be applied only to systems which obey eq 28. By combining the theory from ref 7 with eqs 25–28, eqs 15–16 from section 2 are replaced by

$$\tilde{r}_u^\pm = \frac{r_{S-P+u}^\pm}{\sigma_{S-P+u,u}} = (\sigma_{S-P+u,u})^{-1} \varphi_{S-P+1}((\mathcal{A}_i)) k_{S-P+1}^\pm \prod_{i=1}^M (\mathcal{A}_i)^{\alpha_{iS-P+1}^\pm} \prod_{i=1}^J (\mathcal{X}_i)^{\beta_{iS-P+1}^\pm} \quad (29)$$

$$k_\ell^+ / k_\ell^- = \prod_{i=1}^M (\mathcal{A}_i)^{a_{i\ell}} \prod_{i=1}^J (\mathcal{X}_i)^{b_{i\ell}} \quad \ell = 1, \dots, S - P \quad (30)$$

By eliminating the activities of the active intermediates from eqs 29–30, we get the following expressions for the forward and backward overall reaction rates

$$\tilde{r}_u^\pm = \tilde{k}_u^\pm \varphi_{S-P+u}((\mathcal{A}_i)) \prod_{i=1}^M (\mathcal{A}_i)^{n_{iu}^\pm} \quad (31)$$

where the overall rate coefficients  $\tilde{k}_u^\pm$  and the overall reaction orders  $n_{iu}^\pm$  are given by eqs 18 and 19, respectively. From eq 31, we notice that the equilibrium conditions for the overall reactions lead to the general Horiuti eq 24, which are valid for ideal as well as nonideal systems.

If the rate coefficients at infinite dilution for the elementary reactions obey the Arrhenius relations

$$k_\ell^\pm = v_\ell^\pm \exp(-E_\ell^\pm / RT), \quad (32)$$

the same is true for the overall rate coefficients

$$\tilde{k}_u^\pm = \tilde{v}_u^\pm \exp(-\tilde{E}_u^\pm / RT), \quad (33)$$

where the overall pre-exponential factors  $\tilde{\nu}_u^\pm$  and overall activation energies  $\tilde{E}_u^\pm$  are given by

$$\tilde{\nu}_u^\pm = \frac{\nu_{S+P-u}^\pm}{\sigma_{S+P-u,u}} \prod_{\ell=1}^{S-P} \left( \frac{\nu_\ell^+}{\nu_\ell^-} \right)^{\sum_{i=1}^{S-P} (\mathbf{B}_{S-P,S-P})_{i,\ell}^{-1} \beta_{i,S-P+u}^\pm} \quad (34)$$

$$\tilde{E}_u^\pm = E_{S-P+u}^\pm + \sum_{i=1}^{S-P} \sum_{\ell=1}^{S-P} (E_\ell^+ - E_\ell^-) (\mathbf{B}_{S-P,S-P})_{i,\ell}^{-1} \beta_{i,S-P+u}^\pm \quad (35)$$

The Van't Hoff reaction isochores for the overall reactions are given by

$$\partial \tilde{K}_u^{\text{eq}} / \partial T = \Delta \tilde{H}_u / RT^2 \quad (36)$$

where  $\Delta \tilde{H}_u$  is the thermal effect attached to the  $u$ th overall reaction. From eqs 24, 33, and 36, it follows that

$$\tilde{E}_u^+ - \tilde{E}_u^- = \Delta \tilde{H}_u / \sigma_{S-P+u,u} \quad u = 1, \dots, P \quad (37)$$

Equations 37 are generalizations of the Borekov relation,<sup>6</sup> which is valid for a single-route rate-determining step.

In this section, we have presented a theory of multiple rate-determining steps with multiple overall reactions for nonideal (concentrated) systems. The stoichiometric aspects of the theory are the same as of the theory for ideal systems developed in ref 7 and section 2. A suitable choice for the correction factors  $\varphi_{S-P+u}(\cdot, \cdot)$  (eq 27), leads to results which are formally similar to the ones derived for ideal (diluted) systems in ref 7.

#### 4. Multiple Rate-Determining Steps for Fractal Kinetics

There are both experimental and simulation evidences that there are important differences between “in vivo” and “in vitro” kinetics.<sup>11</sup> Within a cell, usually there is high macromolecular content, even though the concentrations of different macromolecules are rather small. The cellular environment is crowded rather than concentrated because no individual macromolecular species has high concentrations, but the total macromolecular content is significant.<sup>12</sup> Macromolecular crowding reduces the efficiency of the transport processes due to the excluded volume effect as well as due to the occurrence of inhomogeneous structures within the cell. This decrease in reaction efficiency increases as the reaction goes on: the longer the time the higher the decrease of the reaction efficiency. Such a decrease of the reaction efficiency cannot be described by using classical methods, for example, simple models considering activity corrections to the mass action law usually fail. Various new kinetic approaches have been developed for the analysis of reaction kinetics with macromolecular crowding.

A popular approach for describing “in vivo” kinetics was initiated by Kopelman,<sup>13</sup> based on the use of fractal kinetic laws with time-dependent rate coefficients obeying fractal scaling laws of the type

$$k_\ell^\pm \sim t^{-\chi_\ell^\pm} \quad \text{for } t \gg 0 \quad (38)$$

where  $\chi_\ell^\pm$  are fractal exponents between zero and unity and  $t$  stands for time. It has been shown that various models, for example, taking the excluded volume effect into account or geometrical constraints, lead to the same asymptotic scaling laws (eq 38), which are independent of the detailed mechanism of the process. Fractal kinetic laws of type as in eq 38 have a serious limitation: they lead to a singular behavior as  $t \rightarrow 0$ ,

which is physically inconsistent. Recent stimulation studies<sup>11</sup> based on the use of lattice gas reactive automata<sup>14</sup> have shown that slightly modified fractal kinetic laws lead to a best fit of the simulation data for reaction kinetics with macromolecular crowding. These modified fractal kinetic laws remove the singularity for small times. A different solution to this problem which avoids the problem of singular behavior is based on the use of renormalization group approach.<sup>15</sup> If we apply these approaches to the elementary reactions (eq 1), we obtain a set of rate equations of the type

$$r_\ell^\pm = k_\ell^\pm \psi_\ell^\pm(\chi_\ell^\pm, t) \prod_{i=1}^M [\mathbf{A}_i]^{\alpha_i^\pm} \prod_{i=1}^J [\mathbf{X}_i]^{\beta_i^\pm} \quad \ell = 1, \dots, S, \quad (39)$$

where  $\psi_\ell^\pm(\chi_\ell^\pm, t)$  are scaling functions which obey the constraints

$$\psi_\ell^\pm(\chi_\ell^\pm, t) \sim 1 \quad \text{for } t \sim 0 \quad (40)$$

$$\psi_\ell^\pm(\chi_\ell^\pm, t) \sim (\tau_\ell^\pm / t)^{-\chi_\ell^\pm} \quad \text{for } t \gg 0; \quad (41)$$

$\tau_\ell^\pm$  are characteristic time scales which describe the decay of the rate coefficients. The products  $k_\ell^\pm \psi_\ell^\pm(\chi_\ell^\pm, t)$  are time-dependent rate coefficients, and  $k_\ell^\pm$  are classical rate coefficients, corresponding to the limit  $t \rightarrow 0$ . Consistency with thermodynamic equilibrium requires that

$$\chi_\ell^+ = \chi_\ell^- = \chi_\ell \quad (42)$$

$$\tau_\ell^+ = \tau_\ell^- = \tau_\ell \quad (43)$$

$$\psi_\ell^+(\chi_\ell^+, t) = \psi_\ell^-(\chi_\ell^-, t) = \psi(\chi_\ell, t). \quad (44)$$

Simulations based on lattice-gas-reactive automata<sup>11</sup> lead to the following expressions for the scaling functions  $\psi(\chi_\ell, t)$

$$\psi(\chi_\ell, t) = [\tau_\ell / (\tau_\ell + t)]^{\chi_\ell} \quad (45)$$

Renormalization group theory leads to<sup>15</sup>

$$\psi(\chi_\ell, t) = \frac{1}{\Gamma(\chi_\ell)} \left( \frac{\tau_\ell}{t} \right)^{\chi_\ell} \gamma \left[ \chi_\ell \frac{t}{\tau_\ell} (\chi_\ell \Gamma(\chi_\ell))^{1/\chi_\ell} \right] \quad (46)$$

where  $\gamma(a, x) = \int_0^x x^{a-1} \exp(-x) dx$ ,  $a, x > 0$  and  $\Gamma(a) = \int_0^\infty x^{a-1} \exp(-x) dx$ ,  $a > 0$  are the incomplete and complete gamma functions, respectively. Both scaling functions, eqs 45 and 46, have similar properties; they both obey the constraints of eqs 40 and 41 for short and long times, respectively. Their numerical values for intermediate times, although not identical, are close to each other.

We notice that the generalized fractal kinetic laws (eq 39) share a similar structure with nonideal kinetic laws (eq 25) introduced in the preceding section. The rate-determining-step approximation can be easily extended to fractal kinetics. The overall rate equations are

$$\tilde{r}_u^\pm = \tilde{k}_u^\pm \psi_{S-P+u}(\chi_{S-P+u}, t) \prod_{i=1}^M [\mathbf{A}_i]^{n_{iu}^\pm} \quad (47)$$

where the overall rate coefficients  $\tilde{k}_u^\pm$  and the overall reaction orders are given by eqs 18–19. We notice that eqs 47 have a similar structure with eqs 31 derived in the preceding section for nonideal kinetics. Because of this similarity, many results



derived in the preceding section for nonideal kinetics are also valid for fractal kinetics. In particular, the generalized Horiuti relations (eq 24), eqs 33–35 for the temperature dependence of the overall rate coefficients, as well as the generalized Boreskov relations (eq 37) are also valid for fractal kinetics.

In this section, we have derived a theory of the rate-determining steps with multiple overall reactions with fractal kinetics. Although the chemistry of the systems is different, the overall kinetic equations share common features with the approach for concentrated (nonideal) systems developed in section 3, and many theoretical results, including the generalized Horiuti and Boreskov eqs 24 and 37, apply to both systems.

## 5. Conclusions

In this paper, we have shown that the theory of multiple rate-determining steps for systems with multiple overall reactions can be easily extended to concentrated (nonideal) chemical systems as well as to systems for which the elementary reactions obey fractal kinetics. We have arrived at the surprising conclusion that, even though the kinetics is different for the two types of systems, the overall evolution equations share a common structure. In both cases, we choose to express the rate coefficients as products of their limit values for small concentrations or large times, respectively, time-scaling functions expressing the activity or fractal corrections, respectively. Because of this choice, many theoretical results, such as the generalized Horiuti relations (eq 24) and the generalized Boreskov relations (37), concerning the rate coefficients are identical for ideal systems, nonideal (concentrated) systems and systems with fractal kinetics.

This unitary formulation of the theory of rate-determining steps for systems with multiple overall reactions is very convenient for the analysis of experimental data. For example, the method of selecting suitable reaction mechanisms based on the evaluation of the stoichiometric numbers of the rate-determining steps from experimental data can be easily extended to nonideal or fractal kinetics. Whether the systems obey ideal, nonideal, or fractal kinetics, the stoichiometric numbers of the rate-determining steps can be extracted from measured data by applying the same generalized Horiuti or Boreskov equations.

**Acknowledgment.** We dedicate this article to Professor Michel Boudart in honor of his 80<sup>th</sup> birthday. Throughout his distinguished scientific career, Professor Boudart has made important contributions to the theory of reaction routes and its practical applications in chemical kinetics and chemical engineering; these topics are closely related to the subject of our paper. This research has been supported in part by the National Science Foundation.

## List of Symbols

### Uppercase

$A_i$	stable chemical species
$X_i$	active chemical species (reactive intermediates)
$M$	total number of stable species
$J$	total number of active species
$S$	total number of elementary steps
$P$	total number of reaction routes
$\mathcal{K}$	rank of the stoichiometric matrix
$[A_i]$ and $[X_i]$	concentrations of $A_i$ and $X_i$
$\mathcal{A}_i$ and $\mathcal{X}_i$	thermodynamic activities of $A_i$ and $X_i$

$(\cdot \cdot \mathcal{A}_i)$  and  $(\cdot \cdot \mathcal{X}_i)$

vectors of the activities  $A_i$  and  $X_i$

### Lowercase

$\alpha_{i/}^{\pm}$	stoichiometric coefficients of the stable species in the right-hand/left-hand side of elementary step $/$
$\beta_{i/}^{\pm}$	stoichiometric coefficients of the reactive species in the right-hand/left-hand side of elementary step $/$
$\sigma_{/}$	stoichiometric number of elementary step $/$
$\sigma_{u/}$	stoichiometric number of elementary step $/$ within route $u$
$k_{/}^{\pm}$	rate coefficients of the forward/backward (left-to-right/right-to-left) elementary reactions of step $/$
$a_{i/}$	elements of the stable species partition of the stoichiometric matrix
$b_{i/}$	elements of the active species partition of the stoichiometric matrix
$f_{i/}$	generic elements of the stoichiometric matrix
$r_{/}$	net reaction rate of step $/$
$r_{/}^{\pm}$	rates of the forward/backward elementary reactions of step $/$
$\tilde{r}_u$	net overall reaction rate pertaining to route $u$
$\tilde{r}_u^{\pm}$	rates of the forward/backward overall reactions pertaining to route $u$
$\alpha_{i,S-P+u}^{\pm}$	stoichiometric coefficients of stable species in the right-hand/left-hand sides of the rate-determining steps
$\beta_{i,S-P+u}^{\pm}$	stoichiometric coefficients of active species in the right-hand/left-hand sides of the rate-determining steps
$\sigma_{S-P+u,u}$	stoichiometric number of the rate-determining step of route $u$
$n_{iu}^{\pm}$	stable species overall reaction orders in route $u$
$\tilde{k}_u^{\pm}$	rate coefficients of the forward/backward overall reactions pertaining to route $u$
$\tilde{K}_u^{eq}$	equilibrium constant of the overall reaction $u$
$\chi_{/}^{\pm}$	fractal exponents associated with the rate coefficients of step $/$
$\psi_{/}^{\pm}(\chi_{/}^{\pm}, t)$	scaling functions for the rate coefficients of step $/$
$\tau_{/}^{\pm}$	characteristic time scales for the decay of the rate coefficients of step $/$
$t$	time
$\nu^{\pm}/\tilde{\nu}^{\pm}$	pre-exponential factors for elementary/overall reactions
$E_{/}^{\pm}/\tilde{E}_u^{\pm}$	activation energies for elementary/overall reactions
$\gamma(a, x)$	incomplete gamma function

### Vectors and Matrices

$\mathbf{a}_M^{(j)}$	stoichiometric vectors pertaining to stable species
$\mathbf{b}_J^{(j)}$	stoichiometric vectors pertaining to active species
$\mathbf{f}_{M+J}^{(j)}$	stoichiometric vectors (columns of the stoichiometric matrix)
$\mathbf{F}_{M+J,S}$	stoichiometric matrix
$\mathbf{A}_{M+J,S}$	stable species partition of the stoichiometric matrix
$\mathbf{B}_{M+J,S}$	active species partition of the stoichiometric matrix

$\alpha_{M;P}^{\pm}$	matrices of the right-hand side/left-hand side stoichiometric coefficients of stable species in the P rate-determining steps
$\beta_{M;P}^{\pm}$	matrices of the right-hand side/left-hand side stoichiometric coefficients of active species in the P rate-determining steps
$\mathbf{n}_{M;P}^{\pm}$	matrices of the forward/backward overall reaction orders

#### Subscripts and Superscripts

<i>I</i> subscript	running index for chemical species
/subscript	running index for elementary steps
( <i>h</i> ) superscript	running index for stoichiometric vectors
<i>u</i> subscript	running index for routes and overall reactions
elementary reaction	a reaction completely described mechanistically by its stoichiometric equation <sup>4</sup>
elementary step	a pair of forward/backward elementary reactions
complex reaction mechanism	chemical transformation taking place within a system containing stable and active species by means of elementary steps (reaction network)
reaction route	component of a complex reaction with 2-fold meaning: (1) a mass balance equation linking (some of) stable species (overall stoichiometric equation) and (2) a linear combination of elementary steps (reaction submechanism) resulting in canceling of the active species
stoichiometric numbers	sets of integers (the choice of which is not unique) used in linear combinations to obtain reaction routes
rate-determining step	a nonequilibrated step of a reaction route; if a rate-determining step exists, it is the one and only nonequilibrated step of the sequence, all other being quasiequilibrated; see refs 1–6
Horiuti–Nakamura theorem	a proven <sup>2</sup> relationship linking the number of reaction steps, <i>S</i> , reaction routes, <i>P</i> , and independent reaction intermediates, <i>I</i> , of a complex (multiroute) reaction

Horn complexions	products of powers of intermediates' concentrations, used to calculate overall rates when the number of active species is higher than the rank of their corresponding partition of the stoichiometric matrix <sup>8</sup>
Horiuti <sup>1</sup> and Boreskov <sup>6</sup> relationships	equations that link kinetics and thermodynamics of an overall single-route reaction by means of the stoichiometric number of the rate-determining step (Boreskov actually used the reciprocal of the stoichiometric number, which he termed "molecularity")

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