Article

Single-Route Linear Catalytic Mechanism: A New, Kinetico-Thermodynamic Form of the Complex Reaction Rate

Gregory S. Yablonsky [1],* , **Denis Constales [2]** and **Guy B. Marin [3]**

[1] McKelvey School of Engineering, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, 63130-4899 MO, USA

[2] Department of Electronics and Information Systems ELIS, Ghent University, B-9052 Gent, Belgium; denis.constales@ugent.be

[3] Laboratory for Chemical Technology, Ghent University, B-9052 Gent, Belgium; guy.marin@ugent.be

* Correspondence: gy@wustl.edu; Tel.: +1-314-935-5786

check for
updates

Abstract: For a complex catalytic reaction with a single-route linear mechanism, a new, kinetico-thermodynamic form of the steady-state reaction rate is obtained, and we show how its symmetries in terms of the kinetic and thermodynamic parameters allow better discerning their influence on the result. Its reciprocal is equal to the sum of n terms (n is the number of complex reaction steps), each of which is the product of a kinetic factor multiplied by a thermodynamic factor. The kinetic factor is the reciprocal apparent kinetic coefficient of the i-th step. The thermodynamic factor is a function of the apparent equilibrium constants of the i-th equilibrium subsystem, which includes the $(n-1)$ other steps. This kinetico-thermodynamic form separates the kinetic and thermodynamic factors. The result is extended to the case of a buffer substance. It is promising for distinguishing the influence of kinetic and thermodynamic factors in the complex reaction rate. The developed theory is illustrated by examples taken from heterogeneous catalysis.

Keywords: kinetico-thermodynamic rate equation; separation of kinetic and thermodynamic factors; driving force

1. Introduction

How do we derive the reaction rate for a complex reaction, e.g., for a complex catalytic reaction? Based on graph theory, this general problem was posed by King and Atman [1] and, then, Volkenstein and Goldstein [2,3]. Yablonsky and Bykov, using graph theory as well, introduced the concept of relationships between the complex reaction rate equation and structure of the detailed mechanism [4,5]; see also the monographs [6,7]. The kinetic equation for a single-route catalytic reaction with a linear mechanism can always be presented in the form (see [1,2]):

$$R = \frac{C_c}{W} \tag{1}$$

in which C_c is the cycle characteristic. It is related to the overall reaction, $C_c = k^+ f^+(C_r) - k^- f^-(C_p)$, in which $k^+ = \prod_s k_s^+$, $k^- = \prod_s k_s^-$, $k^+/k^- = K$. The functions $f^+(C_r)$, $f^-(C_p)$ are the products of the reactant and product concentrations raised to certain powers, assuming that the rate of reaction follows the mass-action law formally, as if the overall reaction were an elementary reaction. The denominator,

W, reflects the detailed mechanism. Physically, it represents a "resistance" to the overall reaction rate by the "resistances" of the individual steps of the catalytic cycle. The term W equals $\sum_l k_l \prod_i C_i^{p_{li}}$ where k_l is the sum of the products of the kinetic parameters of elementary reactions, C_i is a reactant or product concentration, and p_{li} is a positive integer. Equation (1) can be written in one of the following forms:

$$R = \frac{k^+ \left(f^+(C_r) - \dfrac{f^-(C_p)}{K} \right)}{W} \tag{2}$$

$$R = \frac{k^+ \left(f^+(C_r) - \dfrac{f^-(C_p)}{K} \right)}{\sum_l k_l \prod_i C_i^{p_{li}}} \tag{3}$$

or using the phenomenological forms (see Equation (5.63) in [8]):

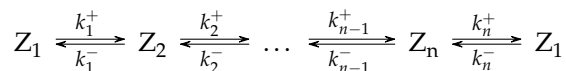$$\text{Reaction Rate} = \frac{\text{Driving Force}}{\text{Kinetic Resistance}} \tag{4}$$

and:

$$\text{Kinetic Resistance} = \frac{\text{Driving Force}}{\text{Reaction rate}} \tag{5}$$

where the expression $f^+(C_r) - f^-(C_p)/K$ is a "driving force". Equations (4) and (5) are very similar to the well-known Ohm's Law considering the analogy between the reaction rate and current and between kinetic "driving force" and voltage as well.

2. Results

2.1. Formulation of the Problem

$$Z_1 \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} Z_2 \underset{k_2^-}{\overset{k_2^+}{\rightleftarrows}} \cdots \underset{k_{n-1}^-}{\overset{k_{n-1}^+}{\rightleftarrows}} Z_n \underset{k_n^-}{\overset{k_n^+}{\rightleftarrows}} Z_1$$

Applying Equation (3) to this mechanism, the equation for the rate can also be written in the form:

$$\frac{1 - \dfrac{Q}{K}}{R} = \sum_i \frac{T_i}{\tilde{k}_i} \tag{6}$$

where $Q = f^+(C_r)/f^-(C_p)$ is the quotient of the overall reaction and K is its equilibrium constant. The expression $(1 - Q/K)$ is a driving force, which does not depend on the details of the mechanism, but only on the overall reaction. As for $\tilde{k}_i$, it is the apparent forward rate constant of the i-th step, which can include the concentration of a gas substance as a parameter. Furthermore, T_i is a function obtained under the assumption that all steps except for the i-th one are under equilibrium conditions. Therefore, every i-th step is characterized by the ensemble of equilibrium reactions. Previously, the concept of the ensemble of equilibrium subsystems was proposed as an efficient method for the mathematical analysis of nonlinear models (see the monographs [8–10] and the papers [11,12]). In fact, the concept of equilibrium subsystems is a generalization of the physico-chemical concept of the equilibrium step, which is well accepted in chemical kinetics. An equilibrium subsystem can be defined by two requirements: that $(n-1)$ steps are at equilibrium and that one step is rate limiting. In the papers [9,10], it was shown that the solutions of these n equilibrium subsystems (i.e., all roots, not just one root) determine the coefficients of the kinetic

polynomial. In the theory of steady-state kinetic models, the kinetic polynomial is the general description of a single-route catalytic reaction.

2.2. Research Analysis

The advantage of Equation (6) is that it is fully symmetric in the mechanism's parameter values, every term presenting the product of a pure kinetic factor $1/\tilde{k}_i$ by a purely thermodynamic term T_i. If one or more steps are irreversible, $K = \infty$ and $\frac{1}{R} = \sum_i \frac{T_i}{\tilde{k}_i}$.

Proof of Equation (6). For this proof, we assume that all gas concentrations are absorbed in the apparent rate constants, so that the mechanism is of the form $Z_1 \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} Z_2 \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \cdots \underset{k_{n-1}^-}{\overset{k_{n-1}^+}{\rightleftharpoons}} Z_n \underset{k_n^-}{\overset{k_n^+}{\rightleftharpoons}} Z_1$, with global quotient $Q = 1$. The rate of the i-th step is denoted R_i and the i-th intermediate as Z_i; we also write $[a]$ for the value in $\{1, \ldots, n\}$ that is equal to a modulo n. We then have that $R_i = k_i^+ Z_i - k_i^- Z_{[i+1]}$; the equilibrium constant of the i-th step is $K_i = k_i^+/k_i^-$, and the balance of intermediates is $Z_1 + \cdots + Z_n = 1$. In terms of $(n+1) \times (n+1)$ matrices, for instance, when $n = 4$,

$$\begin{pmatrix} k_1^+ & -k_1^- & 0 & 0 & R_1 \\ 0 & k_2^+ & -k_2^- & 0 & R_2 \\ 0 & 0 & k_3^+ & -k_3^- & R_3 \\ -k_4^- & 0 & 0 & k_4^+ & R_4 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{7}$$

The determinant of the square matrix must therefore be zero. Expanding it along the rightmost column, $a_1 R_1 + \cdots + a_n R_n = 1$ must hold for some values $a_1, \ldots, a_n$. The equilibrium rate of the i-th step being denoted $R_{i,e}$, by definition, one must have that $a_i = 1/R_{i,e}$; consequently, $\frac{1}{R} = \sum_{i=1}^n \frac{1}{R_{i,e}}$. Calculating the coefficients a_i from the determinant,

$$\frac{1 - \frac{Q}{K}}{R} = \sum_{i=1}^n \frac{1}{\tilde{k}_i}\left(1 + \frac{1}{K_{[i-1]}} + \frac{1}{K_{[i-1]}K_{[i-2]}} + \cdots + \frac{1}{K_{[i-1]} \cdots K_{[i-(n-1)]}}\right) = \sum_{i,j=1}^n \frac{T_{ij}}{\tilde{k}_i}, \tag{8}$$

where $T_{ij} = \dfrac{1}{\prod_{k=1}^{j-1} K_{[i-k]}}$. The concentrations then are determined by:

$$\frac{1 - \frac{Q}{K}}{R} Z_j = \sum_{i=1}^n \frac{T_{i,[i-j+1]}}{\tilde{k}_i}. \tag{9}$$

□

2.3. Special Cases

2.3.1. Single-Route Catalytic Reaction: All Reactions Are Irreversible

In this case, Equation (6) is extremely simplified;

$$\frac{1}{R} = \sum_{i=1}^{n} \frac{1}{\tilde{k}_i} \tag{10}$$

2.3.2. Single-Route Catalytic Reaction: One Step Is Irreversible and Rate Limiting.
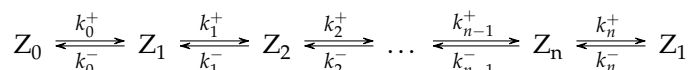
Assuming that the rate limiting step's $1/\tilde{k}_l$ is so large that the other terms with $i \neq l$ can be neglected,

$$\frac{1}{R} = \frac{1}{\tilde{k}_l} \sum_{j=1}^{n} T_{lj} \tag{11}$$

2.4. Extension of the Single-Route Result: Application to Other Mechanisms

2.4.1. Single-Route Catalytic Reaction with a Buffer Step

Let Z_0 be a buffer attached to Z_1. In the steady-state, the reaction step between Z_0 and Z_1 must be balanced; hence, $Z_0 = Z_1/K_0$ always.

$$Z_0 \underset{k_0^-}{\overset{k_0^+}{\rightleftharpoons}} Z_1 \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} Z_2 \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \cdots \underset{k_{n-1}^-}{\overset{k_{n-1}^+}{\rightleftharpoons}} Z_n \underset{k_n^-}{\overset{k_n^+}{\rightleftharpoons}} Z_1$$
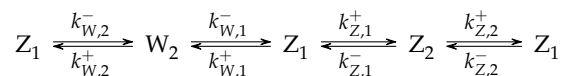
This is reflected in the formulas:

$$\frac{1 - \dfrac{Q}{K}}{R} = \frac{1}{\tilde{k}_1}\left(1 + \frac{1}{K_2} + \frac{1}{K_0}\right) + \frac{1}{\tilde{k}_2}\left(1 + \frac{1}{K_1} + \frac{1}{K_0 K_1}\right) \tag{12}$$

when $n = 2$, and for general n,

$$\frac{1 - \dfrac{Q}{K}}{R} = \sum_{i,j=1}^{n}\left(1 + \frac{\delta_{ij}}{K_0}\right)\frac{T_{i,[i-j+1]}}{\tilde{k}_i}, \quad \frac{1 - \dfrac{Q}{K}}{R}Z_0 = \frac{1}{K_0}\sum_{i=1}^{n}\frac{T_{i,i}}{\tilde{k}_i}, \quad \frac{1 - \dfrac{Q}{K}}{R}Z_j = \sum_{i=1}^{n}\frac{T_{i,[i-j+1]}}{\tilde{k}_i}, \quad j = 1,\ldots,n. \tag{13}$$

2.4.2. Two Cycles that Have a Common Intermediate

For $n = 2$, see [8],

$$Z_1 \underset{k_{W,2}^+}{\overset{k_{W,2}^-}{\rightleftharpoons}} W_2 \underset{k_{W,1}^+}{\overset{k_{W,1}^-}{\rightleftharpoons}} Z_1 \underset{k_{Z,1}^-}{\overset{k_{Z,1}^+}{\rightleftharpoons}} Z_2 \underset{k_{Z,2}^-}{\overset{k_{Z,2}^+}{\rightleftharpoons}} Z_1$$
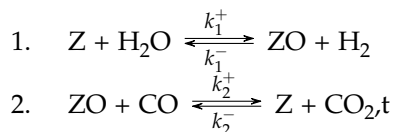
and:

$$\frac{1 - \dfrac{Q}{K}}{R_Z} = \frac{1}{k_{Z,1}^+}\left(1 + \frac{1}{K_{Z,2}}\right) + \frac{1}{k_{Z,2}^+}\left(1 + \frac{1}{K_{Z,1}}\right) + \left(\frac{1}{k_{W,2}^+} + \frac{1}{k_{W,1}^+ K_{W,2}}\right)\frac{\dfrac{1}{k_{Z,1}^+} + \dfrac{1}{k_{Z,2}^+ K_{Z,1}}}{\dfrac{1}{k_{W,1}^+} + \dfrac{1}{k_{W,2}^+ K_{W,1}}}. \tag{14}$$

2.5. Examples

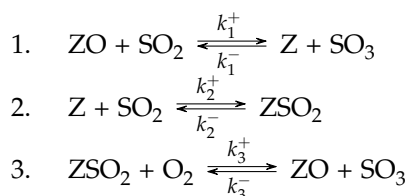2.5.1. Two Step Single Route Mechanism (Water-Gas Shift Mechanism)

1. $Z + H_2O \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} ZO + H_2$

2. $ZO + CO \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} Z + CO_2, t$

where Z is the active catalytic center.
　　The overall reaction is $CO + H_2O \rightleftharpoons CO_2 + H_2$:

$$\frac{1 - \dfrac{Q}{K}}{R} = \frac{1}{\tilde{k}_1^+}\left(1 + \frac{1}{\tilde{K}_2}\right) + \frac{1}{\tilde{k}_2^+}\left(1 + \frac{1}{\tilde{K}_1}\right) \tag{15}$$

where $\tilde{k}_1^+ = k_1^+ C_{H_2O}$, $\tilde{k}_2^+ = k_2^+ C_{CO}$, $\tilde{K}_1 = (k_1^+ C_{H_2O})/(k_1^- C_{H_2})$, $\tilde{K}_2 = (k_2^+ C_{CO})/(k_2^- C_{CO_2})$ and $Q = (C_{CO_2} C_{H_2})/(C_{CO} C_{H_2O})$.

2.5.2. Three Step Mechanism of Sulfur Dioxide Oxidation

1. $ZO + SO_2 \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} Z + SO_3$

2. $Z + SO_2 \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} ZSO_2$

3. $ZSO_2 + O_2 \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} ZO + SO_3$

　　The overall equation is $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$.

$$\frac{1 - \dfrac{Q}{K}}{R} = \frac{1}{\tilde{k}_1^+}\left(1 + \frac{1}{\tilde{K}_3} + \frac{1}{\tilde{K}_3 \tilde{K}_2}\right) + \frac{1}{\tilde{k}_2^+}\left(1 + \frac{1}{\tilde{K}_1} + \frac{1}{\tilde{K}_1 \tilde{K}_3}\right) + \frac{1}{\tilde{k}_3^+}\left(1 + \frac{1}{\tilde{K}_2} + \frac{1}{\tilde{K}_2 \tilde{K}_1}\right) \tag{16}$$

where $\tilde{k}_1^+ = k_1^+ C_{SO_2}$, $\tilde{k}_2^+ = k_2^+ C_{SO_2}$, $\tilde{k}_3^+ = k_3^+ C_{O_2}$, $\tilde{K}_1 = (k_1^+ C_{SO_2})/(k_1^- C_{SO_3})$, $\tilde{K}_2 = (k_2^+ C_{SO_2})/k_2^-$, $\tilde{K}_3 = (k_3^+ C_{O_2})/(k_3^- C_{SO_3})$; $Q = C_{SO_3}^2/(C_{O_2} C_{SO_2}^2)$.

3. Discussion

　　The new kinetico-thermodynamic expressions for the complex catalytic reaction rate presented here, Equation (8) and similar ones, are convenient for analyzing different aspects of kinetic behavior.

　　First, it is possible to characterize the contributions of different steps because the proposed expression is a sum of terms that correspond to different steps. Based on this expression, the problem of distinguishing the domain of validity of a rate limiting assumption can be posed, at least qualitatively [13].

　　In a special case, if all steps are irreversible, the answer is obvious (see Equation (10)), and the *i*-th reaction will be limiting as $\tilde{k}_i$ tends to zero. Generally, two interwoven problems arise: Which step is rate limiting? What is the domain of the validity of the rate limiting assumption?

　　It is possible to simplify Equation (8) by reducing the number of terms that correspond to different steps. Our qualitative analysis shows that a step can be eliminated when both the apparent forward kinetic parameter and the apparent equilibrium constant are large enough. However, it is possible that some step may have a moderate (finite) equilibrium constant despite having both the kinetic parameters, forward and reverse, large. In this case, the corresponding rate term of this step can be eliminated,

but the equilibrium parameter of this step will remain present in the other rate terms. In most cases, determining the rate-determining step requires an analysis based on concrete parameters.

Every term of Equation (8) is an explicit function of the temperature and concentrations: the apparent kinetic coefficient $\tilde{k}_i$ is characterized by an Arrhenius dependence on the temperature and a linear dependence on the gas concentration, and the thermodynamic term T_i is a function of the temperature as well: it is increasing or decreasing with temperature if all present steps are exothermic or endothermic, respectively. Regarding the concentration dependences, T_i is proportional to the reactant concentrations and inversely proportional to the product concentrations.

4. Conclusions

A new, kinetico-thermodynamic form expressing the rate of a complex catalytic single route equation is obtained. According to this form, the reciprocal rate equals the sum of n terms (n is the number of steps), and every i-th term equals the product of the i-th kinetic factor, i.e., the reciprocal i-th apparent kinetic coefficient, multiplied by the i-th apparent thermodynamic term. The latter is a function of the apparent equilibrium constants of the $(n - 1)$ other steps. Generally, the kinetico-thermodynamic form separates kinetic and thermodynamic factors. This form allows estimating the contribution of every step from both kinetic and thermodynamic aspects.

References

1. King, E.; Altman, C. A schematic method of deriving the ratelaws for enzyme-catalyzed reactions. *J. Phys. Chem.* **1956**, *60*, 1375–1378. [CrossRef]
2. Volkenstein, M.V.; Goldstein, B.N. A new method for solving the problems of the stationary kinetics of enzymological reactions. *Biochim. Biophys. Acta* **1966**, *115*, 471–477. [CrossRef]
3. Volkenstein, M.V.; Goldstein, B.N. Method for derivation of enzyme kinetics equations. *Biokhimiya* **1966**, *31*, 541–547. (In Russian)
4. Yablonskii, G.S.; Bykov, V.I. Structured kinetic equations of complex catalytic reactions. *Dokl. Akad. Nauk SSSR* **1977**, *238*, 645–648.
5. Yevstignejev, V.A.; Yablonskii, G.S.; Bykov, V.I. A General steady-state kinetic equation (multi-route linear catalytic mechanism). *Dokl. Akad. Nauk SSSR* **1979**, *245*, 871–874.
6. Yablonskii, G.S.; Bykov, V.I.; Gorban, A.N. *Kinetic Models of Catalytic Reactions*; Nauka: Novossibirsk, Russia, 1983; 256p. (In Russian)
7. Yablonskii, G.S.; Bykov, V.I.; Gorban, A.N.; Elokhin, V.I. *Kinetic Models of Catalytic Reactions*; Compton, R.G., Ed.; Elsevier: Amsterdam, The Netherlands, 1991; 396p.
8. Marin, G.B.; Yablonsky, G.S.; Constales, D. *Kinetics of Chemical Reactions: Decoding Complexity*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2019; 442p.
9. Lazman, M.Z.; Yablonsky, G.S. Overall reaction rate equation of single-route complex catalytic reactions in terms of hypergeometric series. In *Advances in Chemical Engineering—Mathematics in Chemical Engineering and Kinetics*; Marin, G.B., West, D.H., Yablonsky, G.S., Eds.; Elsevier: Amsterdam, The Netherlands, 2008; pp. 47–102.
10. Bykov, V.I.; Kytmanov, A.M.; Lazman, M.Z. In *Elimination Methods in Polynomial Computer Algebra*; Passare, M., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1998; 252p.

11. Lazman, M.Z.; Yablonskii, G.S.; Bykov, V.I. Steady-state kinetic equation (adsorption mechanism of catalytic reaction). *Chem. Fiz.* **1983**, *2*, 413–423. (Translated in *Sov. J. Chem. Phys.* **1985**, *2*, 693–703.)

12. Lazman, M.Z.; Yablonskii, G.S.; Bykov, V.I. Steady-state kinetic equation, Nonlinear single pathway mechanism. *Sov. J. Chem. Phys.* **1985**, *2*, 404–418.

13. Murzin, D. Requiem for the Rate-Determining Step in Complex Heterogeneous Catalytic Reactions? *Reactions* **2020**, *1*, 37–46. [CrossRef]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.