

## SINGLE-ROUTE LINEAR CATALYTIC MECHANISM: A NEW STRUCTURAL FORM OF THE KINETIC EQUATION

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*For a complex catalytic reaction with a single-route linear mechanism, a new form expressing the steady-state rate is obtained: its reciprocal is equal to the sum of  $n$  terms ( $n$  is the number of 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.*

### INTRODUCTION

The kinetic equation for a single-route catalytic reaction with a linear mechanism can always be presented in the form (see [1,2])

$$R = \frac{C_g}{W}, \quad (1)$$

in which  $C_g$  is the cycle characteristic related to the overall reaction,  $C_g = k^+ f^+(c_r) - k^- f^-(c_p)$  where  $k^+ = \prod_s k_s^+$ ,  $k^- = \prod_s k_s^-$ ,  $\frac{k^+}{k^-} = K$ . The functions  $f^+(c_r)$  and  $f^-(c_p)$  are products of reactant and product concentrations raised to a certain power. They are written based on the overall reaction under the assumption that the rate of reaction is governed by the mass-action law as if the overall reaction were an elementary reaction. The term  $W$  can be expressed as  $\sum_i k_i \prod_i c_i^{p_{i_i}}$  where  $k_i$  is a product of kinetic parameters of elementary reactions or a sum of such products,  $c_i$  is a reactant or product concentration and  $p_{i_i}$  is a positive integer. The denominator  $W$  reflects the detailed mechanism. Its physical meaning is a “resistance” or “retardation” of the overall reaction rate by the “resistances” of the individual steps of the catalytic cycle.

### FORMULATION OF THE PROBLEM

The equation for the rate can also be written

$$\frac{1 - \frac{Q}{K}}{R} = \sum_i \frac{T_i}{\bar{k}_i} \quad (2)$$

where  $Q = \frac{f^-(c_p)}{f^+(c_r)}$  is the quotient of the overall reaction, and  $K$  its equilibrium constant. The expression  $1 - \frac{Q}{K}$  is a driving force, which does not depend on the details of the mechanism, but only on the overall reaction. As to  $\bar{k}_i$ , 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 are under equilibrium conditions. Therefore, every  $i$ -th step is characterized by the ensemble of  $(n - 1)$  equilibrium reactions. Previously, the concept of ensemble of equilibrium subsystems was used as a very efficient tool for the mathematical analysis and physico-chemical understanding of nonlinear models (see the monographs [2-4] and the papers [5, 6]). In fact, the concept of equilibrium subsystems is a generalization of the concept of equilibrium step, which is well-known in chemical kinetics. An equilibrium subsystem is a system for which the following assumption holds:  $(n - 1)$  steps are at equilibrium and one step is rate limiting ( $n$  is the number of steps). Then  $n$  of such equilibrium subsystems can be considered. In the theory of nonlinear steady-state kinetic models [4], it was shown that the solutions of these subsystems (all roots, not just one root) define the coefficients of the so-called kinetic polynomial, which is the general form of the steady-state kinetic model of a single-route catalytic reaction.

### RESEARCH ANALYSIS

The advantage of equation (2) is that every term presents the product of a pure kinetic factor  $\frac{1}{\bar{k}_i}$  by a purely thermodynamic term  $T_i$ . If one or more steps are irreversible,  $K = \infty$  and  $\frac{1}{R} = \sum_i \frac{T_i}{\bar{k}_i}$ .

*Proof of equation (2).*

For this proof we assume that all gas concentrations are absorbed in the apparent rate constants, so that the mechanism is of the form  $Z_1 \leftrightarrow Z_2 \leftrightarrow \dots \leftrightarrow Z_n \leftrightarrow Z_1$ , with global quotient  $Q = 1$ . The rate of the  $i$ -th step is denoted  $R_i$  and the  $i$ -th intermediate,  $Z_i$ ; we also write  $[a]$  for the value in  $\{1, \dots, n\}$  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  $Z_1 + \dots + Z_n = 1$ . In terms of  $(n + 1)$  by  $(n + 1)$  matrices, for instance when  $n = 4$ ,

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

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

$$\frac{1 - \frac{1}{K}}{R} = \sum_i \frac{1}{k_i^+} \left( 1 + \frac{1}{K_{[i-1]}} + \frac{1}{K_{[i-1]}K_{[i-2]}} + \dots + \frac{1}{K_{[i-1]} \dots K_{[i-(n-1)]}} \right).$$

Q.E.D.

## CONCLUSIONS

A new form expressing the rate of a complex catalytic single route equation has been 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  $(n - 1)$  apparent equilibrium constants of other steps. This form allows to estimate the contribution of every step from both kinetic and thermodynamic aspects.

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