

A confrontation of the method of quasistationary concentrations with the results derived by means of the Viète theorem

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The relationship between the overall rate constant and the rate constants of particular reaction steps calculated by the method of quasistationary concentrations has been compared with the results obtained by integrating the systems of differential equations of chemical kinetics and with the consequences ensuing from the Viète theorem on roots of an equation. It has been established that the method of quasistationary concentrations is to be regarded as an approximate method for calculating the least (as concerns absolute value) root of the characteristic equation which is valid both for the linear and cyclic sequence of reaction steps.

Зависимость общей константы скорости от констант отдельных ступеней реакции, рассчитанная по методу квазистационарных концентраций, была сравнена с результатами полученными интегрированием систем дифференциальных уравнений химической кинетики и последствиями вытекающими из леммы Вьета о корнях уравнения. Было найдено, что метод квазистационарных концентраций нужно понимать как приближенный метод расчета наименьшего (по абсолютному значению) корня характеристического уравнения, которое остается в силе как для линейной, так и циклической последовательности ступеней реакции.

The method of quasistationary concentrations was introduced into literature by *Bodenstein* [1, 2]. The conditions of its correct use for radical [3, 4] and ionic reactions involving covalent bonds [5] are known. This paper is concerned with the mathematical essence of this method and the possibilities of its extension to reactions the particular reaction steps of which constitute cycles. The comparison of results of the method of quasistationary concentrations with the results obtained by means of the Viète theorem on roots of an equation was used as a method for this study.

Results and discussion

By reason of mathematical formalism, it is useful to classify the reaction systems according to the number of intermediates.

1. System with one intermediate

Let us consider a system in which X , Y , and Z are the reactants, x , y , and z their instantaneous concentrations, and a , b , c the rate constants. The reaction proceeds from starting substances through one intermediate to reaction products according to the following scheme



We assume that all reaction steps obey the law of the first-order reactions. A nucleophilic addition taking place in the presence of excess nucleophilic agent may serve as a practical example of eqn (1).

The reaction system may be described by known kinetic differential eqns (2—4) the solution of which gives characteristic eqn (5). We shall denote its roots by λ_1 and λ_2

$$\frac{-dx}{dt} = ax - by \quad (2)$$

$$\frac{-dy}{dt} = (b + c)y - ax \quad (3)$$

$$\frac{dz}{dt} = cz \quad (4)$$

$$\lambda^2 + \alpha\lambda + \beta = 0 \quad (5)$$

where

$$\alpha = (a + b + c); \quad \beta = ac \quad (6)$$

For instantaneous concentrations of reactants X and Y eqns (7) and (8) are valid [6]. P_1 and Q are integration constants found from boundary conditions

$$\frac{x}{x_0} = P_1[\exp(\lambda_1 t)] + P_2[\exp(\lambda_2 t)] \quad (7)$$

$$\frac{y}{x_0} = -Q[\exp(\lambda_1 t)] + Q[\exp(\lambda_2 t)] \quad (8)$$

For $t = 0$, $x = x_0$, $y = 0$, and $z = 0$, it holds

$$P_1 = \frac{a + \lambda_2}{\lambda_2 - \lambda_1}, \quad P_2 = -\frac{a + \lambda_1}{\lambda_2 - \lambda_1}, \quad Q = \frac{a}{\lambda_2 - \lambda_1}. \quad (9)$$

Dividing eqn (8) by eqn (7), we obtain the ratio y/x . If we assume the time change of y in eqn (3) to be equal to zero we obtain eqn (10) and by combining eqns (10) and (3), we obtain relation (11) for the ratio y/x

$$-\frac{dy}{dt} = 0 \quad (10)$$

$$\frac{y}{x} = \frac{a}{(b+c)} \quad (11)$$

Eqns (10) and (11) are valid for the maximum concentration of intermediate. The method of quasistationary concentrations extends their validity for the time range $t = 0 \rightarrow t = \infty$ and thus it deviates from an exact solution. Supposing a quasistationary concentration of intermediate Y , we obtain eqn (12) from eqns (3) and (10). Thus the relationship between real and quasistationary concentrations is determined in conformity with [7] by eqn (13) where ε is the deviation of quasistationary concentration from real concentration

$$\left(\frac{y}{x}\right)^* = \frac{a}{b+c} \quad (12)$$

$$y = y^*(1 + \varepsilon) \quad (13)$$

Eqn (12) approximates the better to the real ratio of concentrations y/x within the whole time range, the smaller is ε [7]. The ratio $(y/x)/(y/x)^*$ approaches to one the more, the smaller is a in comparison with $(b+c)$ [8]

$$a \ll (b+c) \quad (14)$$

The deviations of the method of quasistationary concentrations from the exact solution were frequently studied in literature [7–10] and therefore we shall discuss them only in the necessary extent. Now, we shall pay attention to the revelation what is the relation between the solution obtained by the method of quasistationary concentrations and the roots of characteristic eqn (5) or integration constants P_i and Q in eqns (7) and (8). By solving eqn (5), we obtain

$$\lambda_{1,2} = \frac{-(a+b+c) \pm \sqrt{(a+b+c)^2 - 4ac}}{2} \quad (15)$$

Because of condition (14), we may write inequality (16) involving inequality (17). As the roots $\lambda_{1,2}$ are negative, inequality (18) is also valid

$$(a+b+c) \gg 4ac \quad (16)$$

$$\lambda_1 \gg \lambda_2 \quad (17)$$

$$|\lambda_1| \ll |\lambda_2| \quad (18)$$

According to the Viète theorem, the roots of characteristic eqn (5) obey eqn (19), but because of inequality (18), eqn (20) is also approximately valid

$$-\alpha = \lambda_1 + \lambda_2; \quad \beta = \lambda_1 \lambda_2 \quad (19)$$

$$-\alpha \doteq \lambda_2 \quad (20)$$

Expression (21) follows from eqns (19) and (20)

$$-\lambda_1 \doteq \beta/\alpha \quad (21)$$

On inserting inequalities (17) and (14) into expressions (9), it is evident that P_1 approximates to one and P_2 and Q to zero with increasing difference of the roots of characteristic eqn (5). Therefore, by maintaining inequalities (17) and (14) and respecting eqn (21), eqn (7) converts into form (22) and the right side of eqn (8) is approximately equal to zero. Simultaneously, the mathematical formalism of the studied reaction changes from complex reaction to isolated reaction

$$\frac{x}{x_0} = \left\{ \exp \left[\frac{-act}{a+b+c} \right] \right\} \quad (22)$$

The method of quasistationary concentrations gives expression (23) if eqns (12) and (2) are combined

$$\left(\frac{x}{x_0} \right)^* = \left\{ \exp \left[\frac{-act}{b+c} \right] \right\} \quad (23)$$

According to this paper, eqn (22) must approximate to eqn (23) the better, the smaller is a with respect to $(b+c)$, as stated by expression (14). The agreement of the results of this study with [7, 8] ensues from these relationships.

2. System with two intermediates

Let us have a system in which a reaction proceeds from reactant X to reaction product W according to scheme (24)



Let us assume that all reaction steps obey the law of the first-order reactions. The reaction system can be described by kinetic differential eqns (25–28)

$$\frac{-dx}{dt} = (a+e)x - by - fz \quad (25)$$

$$\frac{-dy}{dt} = (b+c+g)y - ax - dz \quad (26)$$

$$\frac{-dz}{dt} = (d+f+h)z - ex - cy \quad (27)$$

$$\frac{dw}{dt} = gy + hz \quad (28)$$

This system of differential equations is solvable [11] and leads to characteristic eqn (29)

$$\lambda^3 + \alpha\lambda^2 + \beta\lambda + \gamma = 0 \quad (29)$$

where

$$\alpha = a + b + c + d + e + f + g + h \quad (30)$$

$$\beta = a(c + d + f + g + h) + b(d + e + f + h) + c(e + f + h) + d(e + g) + e(g + h) + g(f + h) \quad (31)$$

$$\gamma = a(ch + dg + fg + gh) + e(bh + ch + dg + gh) \quad (32)$$

The cubic eqn (29) is generally solvable and gives three roots λ_1 , λ_2 , and λ_3 . For instantaneous values of x , y , and z , eqns (33—35) are valid. The values of integration constants P_i , Q_i , R_i may be found from initial conditions. If it holds $t = 0$, $x = x_0$, $y = 0$, and $z = 0$, eqn (36) ensues from eqns (33—35)

$$\frac{x}{x_0} = P_1[\exp(\lambda_1 t)] + P_2[\exp(\lambda_2 t)] + P_3[\exp(\lambda_3 t)] \quad (33)$$

$$\frac{y}{x_0} = Q_1[\exp(\lambda_1 t)] + Q_2[\exp(\lambda_2 t)] + Q_3[\exp(\lambda_3 t)] \quad (34)$$

$$\frac{z}{x_0} = R_1[\exp(\lambda_1 t)] + R_2[\exp(\lambda_2 t)] + R_3[\exp(\lambda_3 t)] \quad (35)$$

$$P_1 + P_2 + P_3 = 1; \quad Q_1 + Q_2 + Q_3 = 0; \quad R_1 + R_2 + R_3 = 0 \quad (36)$$

At given rate constants $a—h$, the calculation of λ_i , P_i , Q_i , R_i makes great demands on tabulated values of cosinus of the angle $89—90^\circ$. Therefore for demonstrating the system of eqns (33—35), it was put $e = f = 0$ and the calculation was performed by means of usual logarithmic tables [12]. The calculated results are summarized in Table 1. Except the tabular error, the calculated values of P_i , Q_i , R_i fulfil eqns (36). It is obvious from Table 1 that inequalities (38) and (39) are valid provided inequality (37) holds. Simultaneously, P_1 approaches the value of one and other integration constants approach zero. Therefore, eqn (33) may be approximated by expression (40) which is formally identical with (22)

$$a \ll b \doteq c \doteq d \doteq g \doteq h \quad (37)$$

$$\lambda_1 \gg \lambda_2 \quad \lambda_1 \gg \lambda_3 \quad (38)$$

$$|\lambda_1| \ll |\lambda_2| \quad |\lambda_1| \ll |\lambda_3| \quad (39)$$

Table 1

Constants of eqns (33—35) as functions of the rate constants of particular reaction steps at $a = 1 \times 10^{-}$ and $e = f = 0$

| $b = c = d = g = h$ | 1×10^{-5} | 1×10^{-4} | 1×10^{-3} | 1×10^{-2} |
|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| $-\lambda_1 \times 10^6$ | 4.6791 | 5.574 | 5.99 | 6.0 |
| $-\lambda_2$ | $1.6527 \times 10^{-}$ | 1.3916×10^{-4} | 1.3840×10^{-3} | 1.3822×10^{-2} |
| $-\lambda_3$ | 3.8794×10^{-5} | 3.6427×10^{-4} | 3.6200×10^{-3} | 3.6182×10^{-2} |
| P_1 | 0.71225 | 0.95289 | 0.99800 | 0.99980 |
| P_2 | 0.20075 | 0.03888 | 0.00145 | 0.00014 |
| P_3 | 0.08592 | 0.00622 | 0.00062 | 0.00005 |
| Q_1 | 0.37903 | 0.04037 | 0.00400 | 0.00040 |
| $-Q_2$ | 0.13103 | 0.01945 | 0.00200 | 0.00020 |
| $-Q_3$ | 0.24740 | 0.02046 | 0.00200 | 0.00020 |
| R_1 | 0.24739 | 0.02087 | 0.00201 | 0.00020 |
| $-R_2$ | 0.37728 | 0.03325 | 0.00325 | 0.00032 |
| R_3 | 0.13164 | 0.01238 | 0.00124 | 0.00012 |

$$\frac{x}{x_0} = [\exp(\lambda_1 t)] \quad (40)$$

Thus from the view-point of kinetic formalism, the complex reaction turns again into isolated reaction of the first order.

If inequality (41) holds in reaction system (24), inequalities (38) and (39) must be simultaneously valid

$$a \doteq e \ll b \doteq c \doteq d \doteq f \doteq g \doteq h \quad (41)$$

According to the Viète theorem, it holds for the roots of eqn (29)

$$\begin{aligned} -\alpha &= \lambda_1 + \lambda_2 + \lambda_3 \\ \beta &= \lambda_1 \lambda_2 + \lambda_1 \lambda_3 + \lambda_2 \lambda_3 \\ -\gamma &= \lambda_1 \lambda_2 \lambda_3 \end{aligned}$$

If inequalities (39) are fulfilled, expressions (42—45) are approximately valid. From eqns (43) and (44), we obtain eqn (45). If inequalities (38) and (39) are fulfilled, eqn (33) assumes the form of eqn (46)

$$-\alpha \doteq \lambda_2 + \lambda_3 \quad (42)$$

$$\beta \doteq \lambda_2 \lambda_3 \quad (43)$$

$$-\gamma = \lambda_1 \lambda_2 \lambda_3 \quad (44)$$

$$-\lambda_1 \doteq \frac{\gamma}{\beta} \quad (45)$$

$$\frac{x}{x_0} = \left\{ \exp \left[\left(\frac{-\gamma}{\beta} \right) t \right] \right\} \quad (46)$$

If we insert from eqns (31) and (32) into eqn (45), we find eqn (47) and by using the method of quasistationary concentrations we obtain eqn (48)

$$-\lambda_1 = \frac{a(ch + dg + fg + gh) + e(bh + ch + dg + gh)}{a(c + d + f + g + h) + b(d + e + f + h) + c(e + f + h) + d(e + g) + e(g + h) + g(f + h)} \quad (47)$$

$$k_{\text{Bod}} = \frac{a(ch + dg + fg + gh) + e(bh + ch + dg + gh)}{(b + g)(d + f + h) + c(f + h)} \quad (48)$$

The numerators of expressions (47) and (48) are equal while the denominators are different only in the terms which contain a and e . Provided inequality (41) is fulfilled, the difference between the denominators of both equations is small and thus eqn (49) is approximately valid, k_{Bod} being the rate constant found by the method of quasistationary concentrations

$$k_{\text{Bod}} \doteq -\lambda_1 \quad (49)$$

From this circumstance, it follows that the mathematical formalism of the method of quasistationary concentrations of all intermediates is to be regarded as an approximate method of calculation of the least (as to the absolute value) root of characteristic equation of the corresponding system of differential equations. By the use of this root and boundary conditions, the value of integration constant is to be found by the method of quasistationary concentrations. The validity of this deduction has been verified for reaction pathways (1) and (24). It may be expected that eqns (40) and (49) are always valid if the process involves a system of the first-order reactions. A comparison of the results obtained on the basis of the Viète theorem with those obtained by the method of quasistationary concentrations gives evidence that this method provides equally accurate results for the systems of linear as well as cyclic reaction steps. Thus it has been demonstrated that the application of the mathematical formalism of the method of quasistationary concentrations to complex reactions the particular reactions of which constitute cycles is equally correct as its application to complex reactions the particular reactions of which proceed in a linear sequence of reaction steps. The use of the method of quasistationary concentrations for reactions of the first order is correct only if the concentration of the starting substance as a function of time fulfils eqn (40) within the scope of experimental errors. This conclusion is in agreement with [5]. As a matter of fact, the dependence of the rate constants of particular reaction steps on conditions of the experiment (pH, composition of solvent, etc.) may be different. Therefore, the dependence of λ_1 on conditions of the experiment may be used as one of the proofs of the complexity of reaction process.

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